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Division of Chemical Science

(IZVESTIYA AKADEMII NAUK SSSR)

(OTDELENIE KHIMICHESKIKH NAUK)

IN ENGLISH TRANSLATION

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INVESTIGATION OF NATURAL SORBENTS BY THE METHOD
OF SMALL-ANGLE SCATTERING OF X RAYS

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The small-angle scattering of x rays is used at the present time for studying regions of heterogeneity in substances. The dimensions of regions of heterogeneity which can be determined by this method usually lie within the range of 10 to 3000 A. The fields of application of this method have been discussed in detail in the monograph of Guinier [1] and the review article of Porai-Koshits [2]. The purpose of the present work was to determine the applicability of the small-angle scattering of x rays to the investigation of natural sorbents of the Far East, which have previously been characterized by various sorption methods [3].

EXPERIMENTAL

For the investigation we used coarsely porous silica gel KSK and two powdered samples of sulfunites,* samples 55 and 223, which had quite high sorption properties.

The frame camera described by Kratky [4] are used. For the work we employed CuK_α radiation, λ = = 1.54 A, monochromated by reflection from a pentaerythritol crystal. The exposure was made with 40 kw and 15 ma. The narrow beam of x rays (0.1 mm) passed from the frame camera to a vacuum fitting containing the sample and the film. The distance from the film to the sample was 195 mm. The cell with the powdered sample, held between two mica windows (sample thickness 0.3-0.4 mm), was fixed on a slide in the vacuum fitting. The x-ray film was also fixed to the slide. The primary x-ray beam was partially absorbed with a trap, consisting of copper foil 0.25 mm thick. The mark of the primary beam on the film facilitated photometric measurements and the adjustment of the camera, and made it possible to approach close to the primary beam so that the minimum angle was 2.82°.

The exposure time varied from 4 to 8 hr, depending on the density and thickness of the sample investigated. Photometric measurements on the x-ray diffraction patterns were made with an MF-2 visual microphotometer. "Agfa" x-ray film was used in the work.

Results of measurements. Figure 1 shows microphotometric curves of scattering intensity of the samples investigated, I, as a function of distance from the primary beam on the film r. Calculations on the x-ray scattering patterns were carried out by the method of tangents [5]. The collimation correction for the slit height was introduced graphically. The corrected curves were calculated with the introduction of a correction for the slit width [6]. The radii of inertia of the regions of heterogeneity were determined from the tangents to the curves of log I against r^2. The intercepts of the tangents on the ordinate axis were used to determine the relative content of the fractions with the dimensions obtained.

The x-ray scattering pattern of KSK was characterized by a weakly expressed maximum, whose position was determined by the method described in [6]. As was shown in [7], the appearance of an interference maximum may be explained by the presence of dense packing in the regions of heterogeneity of radius R with the value $KR = 2.25-2.5$ where $K = 2\pi\varphi/\lambda$, which corresponds to $R = 69.5-77.5$ A for KSK. In view of the high porosity

* Transliteration of the Russian original.
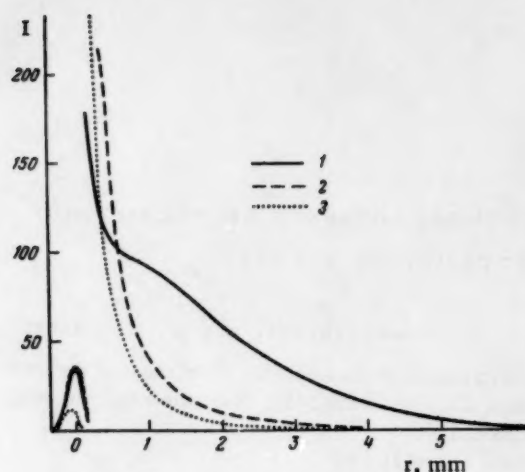
Fig. 1. Microphotometric curves of the scattering intensity (I against $\underline{r}$) of samples: 1) KSK; 2) 223; 3) 55.
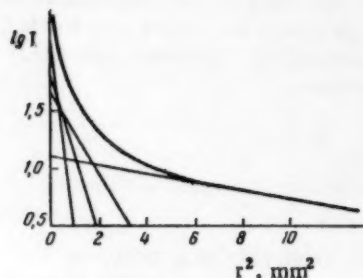
Fig. 2. Calculation by the method of tangents on the scattering intensity curve (log I against r^2) of sample 223.

of silica gel (equal to 69.5% - 77.5 A), it may be considered that the appearance of the maximum is caused by dense packing of the pores of the given dimensions.

The method of tangents, applied to the tail of the graph of log I against r^2, gave only one radius of inertia R due to the almost linear relation and this equaled 29 A, which corresponds to a pore (particle) radius of 37 A. According to [8], the difference in the values of R calculated from the maximum and the "tail" of the logarithmic curve of the intensity is explained by the presence of particles (pores) of different dimensions; in such cases, the calculation from the maximum is recommended.

As a result of analysis of the microphotometric curves of samples 55 and 223 it can be considered that the small-angle scattering of x rays is produced by the presence of loose packing of the regions of heterogeneity (gas type according to Debye) [9]. Figure 2 shows the course of a calculation by the method of tangents on the curve of log I against r^2 of sample 223. The results of calculating the radii of inertia of the samples investigated are given in Table 1.

Determination of specific surface. According to the theory in [1, 2], the small-angle scattering of x rays is caused by the difference in electron density of the particle and medium. This hampers the interpretation of the x-ray scattering patterns, i.e., gives no possibility of deciding on the true nature of the scattering regions (pores or particles). Additional investigations of the samples studied are used to solve this problem. Thus, for example, there is the work [8] where microporous glasses were treated with alkali and the x-ray scattering patterns showed an increase in the dimensions of the scattering regions, which led the authors to the unequivocal conclusion that the scattering was produced by pores.

To some extent, sorption measurements also make it possible to make an analysis of the true nature of the scattering regions and to compare the results of measurements made by two independent methods. In addition to the radii of the regions of heterogeneity, as such a value for comparison we may use the specific surface, which may be calculated approximately from data on small-angle scattering of x rays if we know the "free" volume in a gram of sample, which may be taken as the volume of sorbed vapor in cc/g at $p/p_s = 1$.

TABLE 1

Sample	Radii of regions of heterogeneity in A and their relative content in % on number of particles, obtained by method of tangents									
	A	%	A	%	A	%	A	%	A	%
Coarsely porous silica gel KSK	37	100	77,5*	100	--	—	—	—	—	—
Sample 55	17,3	90,6	71,2	7,25	121	1,63	214	0,410	256	0,11
Sample 223	31	95,6	96	3,92	158	0,738	236	0,282	—	—

* 77.5 A, calculated from maximum.

TABLE 2

Sample	Specific surface in m^2/g						
	calculated from data from method of tangents		calculated from maximum		sorption data [10]		
	particles	pores	particles	pores	for heptane in m^2/g	effective radius of pores in A for heptane	limiting sorption volume in cc/g
Silica gel KSK	121	689	65	328	366	45.5	0.850
Sample 55	250.1	37.65	—	—	45	58	0.130
Sample 223	320	46.5	—	—	40	62	0.124

Above we give the results of comparing the radii of the regions of heterogeneity and the specific surface (Table 2), calculated with the assumption in one case that the scattering was produced by particles and in the other, by pores, with values obtained by sorption measurements by the capillary condensation method with heptane [10]. The specific surface of coarsely porous silica gel was determined from the radii calculated from the maximum and by the method of tangents (for the "tail"). In the determination of the specific surface in this case, it was assumed that there was a monodisperse system of spherical regions of heterogeneity. The specific surface of samples 55 and 223 was calculated considering the relative content of regions of heterogeneity of a given size, which were also considered as spherical. It should be noted that this idealized approach to the determination of the specific surface can only give very approximate results.

As the data in Table 2 show, the specific surfaces of the samples investigated determined from the small-angle scattering of x rays are of the same order as the specific surface determined from sorption data. The specific surface of coarsely porous silica gel calculated from the maximum with the assumption that the scattering was produced by pores agrees reasonably with the specific surface determined from the sorption of heptane vapor, though the radius, which equals 77.5 A in this case, is somewhat higher than 45.5 A, which is the effective radius from the sorption of heptane. For natural sorbents the specific surfaces calculated on the assumption that scattering was produced by pores were also close to the specific surfaces from the sorption of heptane, though the polyphase nature of the natural sorbents, which were mainly a mixture of various aluminosilicates with crystalline SiO_2, requires further investigation.

The results obtained in the investigation of the submicroscopic regions of natural sorbents and silica gel by the method of small-angle scattering of x rays should be considered primarily as supplementary data to the results of other physicochemical methods. The difficulty of applying this method to the study of natural sorbents is caused by the chemical heterogeneity and polyphase structure of the latter. Despite the fact that the

intensity of diffuse scattering at small angles is independent of the internal structure of the scattering regions, the polyphase structure of the natural sorbent must naturally complicate the general picture of small-angle scattering, the full analysis of which is only possible with the aid of other physicochemical methods. In our opinion, the application of the small-angle scattering of x rays to the study of the structure of natural sorbents gives the general features of the dispersion which, with further refinement of x ray analysis procedures in this field, should make it possible to obtain fuller results.

SUMMARY

1. An investigation of the porous structure of coarsely porous silica gel and two samples of natural sorbents is described. The radii of submicroscopic regions of heterogeneity were calculated.

2. The small-angle scattering of x rays was used in an attempt to determine the specific surfaces of the samples studied and the results agreed to a certain extent with sorption data.

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*Original Russian pagination. See C. B. Translation.

CATALYTIC ACTIVITY OF SOLID SOLUTIONS OF NICKELOUS
AND ZINC OXIDES

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The development of the electronic approach to catalysis has stimulated interest in the investigation of the catalytic activity of solid solutions of metal and then of oxides. The electrical conductivity of extrinsic semiconductors, which is connected with their electronic structure, depends on the concentration and disposition of donor and acceptor local electron levels with respect to the level of the valence zone in the electronic scheme. Donor or acceptor local levels are produced by disturbance of stoichiometry or the solution in the lattice of impurities which differ in chemical composition [1]. An example of the first type is stoichiometrically excess oxygen in NiO, where the electrical conductivity depends strongly on its concentration. On dissolving, the oxygen is converted into O^{2-} ions, which lie at the lattice points. To each excess O^{2-} anion there corresponds one vacant cationic point and two Ni^{3+} cations, formed from Ni^{2+} cations after their donation of electrons to the excess oxygen atom. The cationic vacant point in combination with the two Ni^{3+} cations forms an acceptor electron level. On falling from the valence zone, an electron frees an Ni^{3+} cation, i.e., a hole. The electrical conductivity may be varied analogously by dissolving metal oxides in NiO. When LiO_2 is dissolved in NiO, acceptor levels are formed by combination of Li^+ cations with Ni^{3+} cations.

The electrical conductivity of zinc oxide is determined by the content of zinc in excess of the stoichiometric amount. It was established that it is in the form of atoms in interlattice-point positions and forms donor electron levels, as it has a reduced ionization potential equal to 0.1 ev, due to which it readily donates an electron to the conductivity zone. Donor electron levels may also be created by the solution of Ga_2O_3 and other oxides of tri- and higher valent metals in ZnO. Ga^{3+} cations, occupying cationic points in combination with Zn^+ cations, create donor electron levels, whose ionization potential is even lower than that of Zn atoms in interlattice-point positions and therefore they strongly reduce the activation energy of electrical conductivity and increase the electrical conductivity.

The catalytic activity of solid solutions of nickelous and zinc oxides has been widely investigated both in the Soviet Union and abroad. These two systems have become, to a certain extent, models which have been used for testing laws of catalysis and its connection with electrical conductivity for hole and electron semiconductors. Reactions of the oxidation—reduction type have been investigated: the oxidation of CO [2-4], the decomposition of nitrous oxide [3-6], the decomposition of ozone [7], and the exchange of hydrogen and deuterium [8, 9]. In all cases it was found that dissolved impurities had a strong effect simultaneously on the electrical conductivity and the catalytic activity. These data were considered to be in complete agreement with the electronic theory of chemisorption, developed by Vol'kenshtein [10], Hauffe [11], Aigrain [12], Weisz [15], and others [14]. In these investigations the kinetics of the catalytic process were studied very superficially, and as a rule, the step-wise mechanism of the process was not studied. For this reason, a mechanism was usually constructed and a donor or acceptor stage chosen for the slowest one determining the rate of the catalytic process in relation to whether the changes in the electrical conductivity and catalytic activity were symbatic or antibatic [15]. The basis of the construction of the mechanism was the idea stemming from the electronic theory of chemical

$v \cdot 10^3$ cc/m² · min

Fig. 1. Relation between the rate of oxygen adsorption on NiO and its solid solutions and the content of Li^+ and Fe^{+3} cations at the lattice points. The rate is in cc/m² · min and the concentration in atomic % (according to the data of Keier and Kutseva).

adsorption of these authors that the active adsorption centers of gas donors of electrons in p-semiconductors are holes and of gas acceptors of electrons in n-semiconductors are free electrons. The rate of adsorption of gas acceptors of electrons, which is accompanied by a fall in the electrical conductivity of p-semiconductors, should therefore increase with an increase in the initial electrical conductivity of the sample and decrease with a decrease in the latter. The adsorption of gas donors of electrons on p-semiconductors should increase with an increase in their electrical conductivity, as in this case the active centers are assumed to be holes. There has been no experimental test of this fundamental idea, which lies at the basis of this electronic theory of chemisorption and catalysis.

An investigation of the relation between the laws of chemisorption and the initial electrical conductivity of nickelous and zinc oxides, carried out by the author with Kutseva [16, 17] and Chizhikova [18, 19] showed that in practice there are more complex relations and without an understanding of these it is impossible to derive either an electronic theory of chemisorption or a theory of catalysis.

Chemisorption of solid solutions of NiO and ZnO. The laws of the adsorption of gases, which may be divided into electron donors and acceptors according to their effect on the electrical conductivity, were investigated. The adsorption of the donors is accompanied by the transfer of an electron from the adsorbate to the catalyst and the adsorption of the acceptors, by a transfer in the reverse direction; the former are positively charged, and the latter, negatively. The adsorption properties of catalysts change considerably with the solution of oxides of mono- and trivalent metals, which simultaneously affect the electrical conductivity σ of NiO and ZnO; in this case the electrical conductivity σ of ZnO and NiO changes in opposite directions. The solution of lithium oxide in NiO and ZnO increases the initial rate of adsorption of the gas-acceptor oxygen, which passes through a maximum at 0.8 at. % of lithium in NiO and begins to fall with a further increase in concentration. Figure 1 shows the relation between the initial rate of oxygen adsorption and the lithium concentration in NiO. Dissolved Li_2O in NiO and ZnO has an opposite effect on the adsorption of gas donors of electrons, which include acetylene and CO. With a lithium content of 0.4-0.8 at. %, the adsorption of gas donors is completely inhibited. The solution of oxides of trivalent metals, Fe_2O_3, for example, in NiO sharply reduces the rate of oxygen adsorption and simultaneously reduces the rate of CO adsorption slightly. The solution of Ga_2O_3 in ZnO has no effect on oxygen adsorption.

Moreover, there is no direct connection between the activity of the catalyst and the electrical conductivity. With the simultaneous solution of lithium and iron oxides in NiO, the electrical conductivity of NiO is unchanged when their contents are equal. The adsorption properties of an NiO sample containing 0.8 at. % of Li and 0.8 at. % of Fe, and NiO differ considerably. There is no adsorption of gas donors of electrons on the first sample but when there is excess iron oxide relative to Li_2O, when the electrical conductivity is considerably reduced, the capacity to adsorb CO appears despite the fact that, as already noted, the solution of Fe_2O_3 in NiO by itself inhibits CO adsorption. Finally, if the electrical conductivity of NiO is changed by the solution of excess oxygen in the lattice, which acts in the same direction as the solution of Li_2O, preparations are obtained which have the same electrical conductivity as solid solutions of NiO(Li_2O), but differ sharply with respect to chemical adsorption and catalytic activity.

As has already been noted, the solution of Li_2O reduces the rate of adsorption of gas donors of electrons and makes NiO incapable of adsorbing the gases CO and C_2H_2 when the content is 0.4-0.8 at. %; at the same time, excess oxygen in an amount producing the same change in the electrical conductivity and its activation

Fig. 2. Relation between $k = \ln(1/t_{0.5})$ for the oxidation of CO on NiO (0.8 at. % Li) and the reciprocal absolute temperature (according to Sazanova's data).

energy has little effect on the chemisorption of these gases. When Li_2O is dissolved in NiO and ZnO, replacement solid solutions are formed in which some of the cationic lattice points belonging to Ni^{2+} and Zn^{2+} are occupied by Li^+ cations with a reduced charge. At these lattice points, the charge of neighboring oxygen atoms is uncompensated. The cations with an anomalous uncompensated charge create a strong electrostatic field which binds Ni^{3+}, present in NiO in amounts equivalent to the lithium, and interlattice-point (Zn^+) cations in ZnO. The combination of the cations Li^+Ni^{3+} and $Li^+Zn^+_{inter}$ creates acceptor impurity levels, which, being occupied by electrons, free Ni^{3+} cations or holes in NiO and bind free electrons in ZnO; in the first case the electrical conductivity increases and in the second, it falls.

The occupation of an acceptor level by an electron is accompanied by the formation about the lithium cation of an excess negative charge of one electron, which disrupts the periodic potential. It is assumed that the electrostatic field of this charge at the surface reduces the electronic work function at the nearest cationic lattice points occupied by Ni^{2+} cations, which promotes the adsorption of gas-acceptors that abstract electrons, so that close to the Li^+ cation there is produced an Ni^{3+} cation bound by the electrostatic field, while the charge of the opposite sign on the adsorbed molecule reacts with it more weakly due to the greater distance. The closer the Ni^{2+} cation is to the Li^+ cation, the higher is its adsorption capacity. A fall in the activation energy of oxygen adsorption is observed experimentally when Li_2O is dissolved in NiO and ZnO. The initial rate of oxygen adsorption on NiO falls with an increase in the lithium concentration above 0.8 at. %. This fall is due to the reaction between Li^+ cations and Ni^{3+} cations at the maximum distance, which lies at a distance of 2-3 cationic lattice points at this concentration. It is assumed that in ZnO the most active centers for the adsorption of oxygen with a low adsorption activation energy are Zn^+ cations or free electrons on the surface, lying in the zone of influence of the electrostatic field of an O^{2-} anion close to an Li^+ cation with an uncompensated charge. This explains why despite the increase in the space concentration of free electrons when Ga_2O_3 is dissolved in ZnO, the rate of oxygen adsorption does not increase, while when Li_2O is dissolved, despite the fall in free-electron concentration, the rate of oxygen adsorption increases by a factor of several tens due to the reduction in the minimum adsorption activation energy. For quantitative agreement on the effect of dissolved lithium on adsorption by NiO and ZnO it is necessary to assume that each lithium cation on the surface creates not one but several active centers with a low adsorption activation energy.

As will be seen from the following, the catalytic activity of solid solutions of NiO and ZnO is completely determined by the change in the rules of chemisorption due to the change in the nature of the heterogeneity of the active surface when cations with an anomalous charge are introduced into the lattice.

Oxidation of CO. The oxidation of CO on NiO and its solid solutions has been investigated by many authors. Sazonova, Roginskii, and the author [4] established that the solution of lithium oxide in NiO reduces the catalytic activity of NiO with respect to the oxidation of CO. An investigation of the kinetic rules showed that the oxidation rate depends on the CO pressure to a fractional degree close to one half and is independent of the oxygen pressure with a change in the component ratio from a slight deficiency to a multifold excess relative to the stoichiometric ratio. This agrees with the hypothesis that the adsorption of CO is the stage determining the oxidation rate. The data obtained are completely explained by the effect of solution of the oxides Li_2O and Fe_2O_3 on the chemisorption of CO and oxygen, and the mutual effect of the adsorption of oxygen on CO adsorption. The activation energy of CO adsorption could not be measured, but for the analogous gas-donor of electrons, acetylene, the minimum adsorption activation energy increased strongly with the solution of lithium oxide. Parravano [2] also observed a fall in the CO oxidation rate and an increase in the activation energy of this process when Li_2O was dissolved in NiO. The disagreement with the data of Schwab and Block [3], who observed that the solution of Li_2O had the opposite effect on the oxidation of CO, is apparently connected with procedural factors. Judging by the relation of the logarithm of the rate constant of CO oxidation and the reciprocal temperature given by the authors of [3], as in our investigation [4], the NiO(Li_2O) samples had a considerably lower activity than NiO(Cr_2O_3) samples. The activation energies for NiO(Cr_2O_3) and NiO(Li_2O) samples were measured over different

Fig. 3. Relation between the rate of nitrous oxide decomposition on NiO and its solid solutions and the molar content of Li_2O and In_2O_3 (according to the data of Hauffe and Engell) P_{N_2O} = const.

temperature ranges; below 300° for the first and above for the second. The activity of NiO was not measured at all and the data of Parravano were apparently used for it. Sazonova [20] showed that at 325° there is a break on the line showing the relation between the logarithm of the rate constant and the reciprocal absolute temperature (Fig. 2). The activation energy for CO oxidation on NiO(0.8 at. % Li), which equals 17 kcal/mole over the temperature range from 200 to 325°, is reduced to 7 kcal/mole for the temperature range of 325 to 450°. The measurements of Sazonova, Roginskii, and the author [4] on solid solutions of various compositions, were made over the temperature range from room temperature to 350°, in which the activation energy of the oxidation does not change. The solution of Cr_2O_3 in NiO hardly changed the activation energy.

The oxidation of CO on ZnO and its solid solutions was investigated by Chizhikova and the author [18, 19]. The activation energy of CO oxidation was increased by the solution of Li_2O and reduced slightly by the solution of Ga_2O_3. Despite the quantitative discrepancies between these data and those obtained for the same system by Schwab and Block [3], they agree qualitatively. As for NiO, these results may be explained by a reduction in the rate of CO adsorption, as with the solution of 0.5 at. % of Li, there was no adsorption of CO right up to high temperatures. Special experiments showed that adsorption of CO on this sample could be initiated by preliminary adsorption of oxygen. It was established that the oxidation rate on ZnO depends on the oxygen and CO pressure. For a stoichiometric mixture, the first-order law with respect to total pressure was obeyed. The fractional order of the dependence of the oxidation rate on the CO and oxygen pressure indicates a mechanism whereby CO_2 is formed by the interaction of adsorbed CO and O_2. Preliminary adsorption of oxygen, which facilitates the adsorption of CO, nonetheless does not eliminate a fall in the rate of CO adsorption with solution of lithium oxide.

Decomposition of N_2O. The decomposition of nitrous oxide proceeds according to the over-all equation

$$2N_2O \rightarrow 2N_2 + O_2.$$
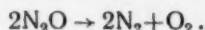
It was established that the electrical conductivity of NiO during the decomposition of N_2O in a mixture with oxygen is higher than in the absence of N_2O under the same conditions [15]. The reverse occurs for ZnO, i.e., there is an increase in electrical conductivity [16]. Judging by these data, nitrous oxide is an electron acceptor. The effect of foreign cations on the decomposition of nitrous oxide depends on the mechanism of the process and the slowest stage.

Decomposition of N_2O on NiO. Hauffe, Engell, and Glang [5] investigated the decomposition of N_2O on NiO and its solid solutions. Solution of Li_2O increased the N_2O decomposition rate. This increase passed through a maximum at approximately 0.5 mol. % of dissolved Li (1 at. % Li), then the rate fell, and at a content of 3 mol. % it became lower than on the starting NiO. The solution of 1 mol. % of In_2O_3 also reduced the activity of NiO with respect to N_2O decomposition. Figure 3 shows curves characterizing the change in N_2O decomposition rate in relation to the indium and lithium content for various temperatures. A comparison of the curves for the relation between the adsorption rate of the gas-acceptor of electrons, oxygen, and the dissolved lithium and iron content of NiO (Fig. 1) with the curves in Fig. 3 shows that they are similar. This makes it probable that the stage limiting the rate of N_2O decomposition is the adsorption of nitrous oxide, whose rate depends on the content of dissolved impurities, similarly to the adsorption of oxygen. This hypothesis is in complete agreement with the first-order dependence of the rate of nitrous oxide decomposition on its pressure, which is observed experimentally. A similar relation between the adsorption of gas-acceptors of electrons and the decomposition of N_2O also exists for ZnO, which is an electron semiconductor.

Decomposition of N_2O on ZnO. Wagner [6] investigated the decomposition of N_2O on ZnO and its solid solution containing 1 mol. % of Ga_2O_3. The solution of Ga_2O_3 increases the electrical conductivity but no effect on the decomposition of N_2O, which was studied above 600°, could be detected. In the later investigation of Schwab and Block [3], it was observed that the solution of LiO_2 in small amounts strongly increased the rate of

N$_2$O decomposition, but with a further increase in the amount of Li$_2$O, the rate fell. The optimal amount of lithium, at which there was the maximum rate of N$_2$O decomposition, lay within the concentration range of 0.5-0.7 mol.% of Li$_2$O. Solution of gallium oxide in ZnO slightly reduced the N$_2$O decomposition rate. Figure 4 shows the relation between the rate of N$_2$O decomposition on ZnO and the content of dissolved lithium and gallium oxides (according to the data of Schwab and Block). According to the data of Chizhikova and the author, for the adsorption of oxygen, in one case for a set of samples of solid solutions of ZnO with lithium oxide a maximum was observed in the initial rate of oxygen adsorption for an Li content of 0.5 at.% [18]. This result was not reproducible later for samples of the same composition prepared from different zinc carbonates. For other sets prepared differently, there was an increase in the initial rate of oxygen adsorption with an increase in the lithium concentration. When the ZnO contained 9 at.% of lithium, the amount of adsorbed oxygen exceeded a monolayer. It is possible that there was volume absorption of oxygen due to the presence of the phase LiZn, which was detected by Kushnarev in an x-ray structural investigation of this sample [19].

The presence of a maximum in the rate of nitrous oxide decomposition at a lithium content of 0.5 at.% may be connected with the correspondence of the samples investigated with those for which a maximum was observed in the oxygen adsorption. However, it is more probable to consider another reason for the observed relation, namely, the poisoning effect of strongly adsorbed oxygen, liberated during the decomposition of nitrous oxide, which reduces the adsorption of N$_2$O on samples containing a higher lithium concentration, on which stronger adsorption of oxygen is observed. Thus, in this case also the complex relations observed in the change in the nitrous oxide decomposition rate may be explained by the change in the rate of N$_2$O adsorption, which is apparently the stage limiting the rate of the catalytic process. This agrees with the first-order dependence of the decomposition rate on the nitrous oxide pressure established experimentally [6]. The rate of N$_2$O decomposition on NiO and ZnO, according to this hypothesis, is limited by the stage of nitrous oxide adsorption. To explain the form of the relation of the N$_2$O decomposition rate to the content of impurities dissolved in NiO and ZnO (Figs. 3 and 4), Hauffe and Schlosser [21] gave a theory for these processes, which contains a number of hypotheses. It was considered that the following stepwise mechanism occurs on NiO:

1) $N_2O + Ni^{2+} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (N_2O)^-_{ads} + (Ni^{3+})_{bound}$

2) $(N_2O)^-_{ads} \overset{k_3}{\rightarrow} (O)^-_{ads} + (N_2)_{gas}$

3) $(N_2O)^-_{ads} + (Ni^{3+})_{bound} + (N_2O)_{gas} \overset{k_4}{\rightarrow} 2(N_2)_{gas} + (O_2)_{gas} + Ni^{2+}$

4) $(O)^-_{ads} + (Ni^{3+})_{bound} + (N_2O)_{gas} \overset{k_5}{\rightarrow} (N_2)_{gas} + (O_2)_{gas} + Ni^{2+}$
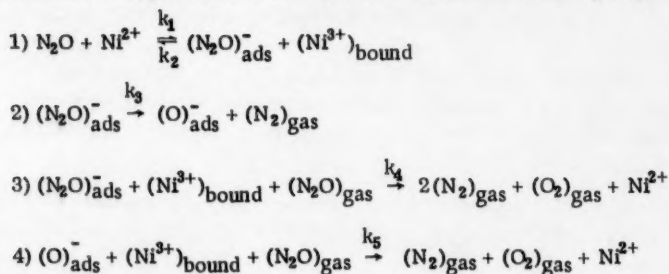
Starting from this stepwise mechanism and with the aid of the stationary concentrations method of Bodenstein, Hauffe and Schlosser derived an equation for the rate of nitrous oxide decomposition involving the Fermi level, characterizing the catalyst, and the local level of a chemisorbed N$_2$O molecule. For the derivation it was essential to introduce the Fermi factor into the reaction of gaseous molecules with the surface. In the opinion of the authors, this factor shows the fraction of N$_2$O molecules on the surface that are not connected with electrons and depends on the ratio of the Fermi level and the local level of the adsorbed molecule. If the local level is higher than the Fermi level, the Fermi factor tends to unity, and if it is lower, the Fermi factor tends to zero. The equation derived for the rate of nitrous oxide decomposition has the following form:

$$\frac{dn_{N_2}}{dt} = KP_{N_2O}\,\gamma \exp\left(-\Delta E_0 e/kT\right)\left[1 - \frac{1}{1 + K_3 \exp\left(\Delta\tau_{i+} - VD\right)e/kT + K_4 P_{N_2O}\,\gamma}\right], \tag{1}$$

where γ is the Fermi factor.
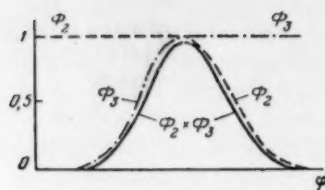
Fig. 5. Change in the factors Φ_2 and Φ_3 from the rate of nitrous oxide decomposition on NiO, according to the theory of Hauffe and Schlosser.

$$\gamma = \frac{1}{1 + \exp\left[\{\Delta\gamma_{i+} - \Delta E_0 - V_D\}\, e/kT\right]}$$

$$\{1 + K_3 \exp(\Delta\gamma_{i+} - V_D)e/kT\} \gg K_4 P_{N_2O}\gamma, \qquad (2)$$

By assuming that
the approximate equation has the form:

$$\frac{dn_{N_2}}{dt} \approx K^* P_{N_2O} \exp(-\varphi_1)\, \Phi_2\Phi_3, \qquad (3)$$

where

$$\varphi = (\Delta\gamma_{i+} - V_D)e/kT; \quad \Delta E_0 e/kT = \varphi_1 \; \text{and} \; \ln 1/K^* = \varphi_2,$$

$$\Phi_2 = \frac{1}{1 + \exp(\varphi - \varphi_1)} \quad \Phi_3 = \frac{1}{1 + \exp(-\varphi + \varphi_2)}.$$

The value of φ depends on the Fermi level and the size of the knee zone connected with adsorption. The factors Φ_2 and Φ_3 depend on φ and change in opposite directions.

Figure 5 shows the change in Φ_2 and Φ_3 in relation to φ. It can be seen that the product of these values passes through a maximum. It should be noted that the authors of this theory examined only the case when the values φ_1 and φ_2 are of the same order but $\varphi_2 > \varphi_1$. If the reverse is the case, i.e., $\varphi_1 > \varphi_2$, then the decomposition rate should equal zero. The factor Φ_2 is connected with adsorption, as it includes the parameter φ, characterizing the height of the local level of the adsorbed molecule. The factor Φ_3 is connected with the desorption process. Thus, the given theory cannot explain the form we observed for the relation of the rate of O_2 adsorption and the LiO_2 content of NiO, presented in Fig. 1.

The authors were unable to explain the acceleration of N_2O decomposition with the solution of Li_2O in the p-semiconductor ZnO. According to their equation there should be an acceleration of the decomposition with solution of Ga_2O_3. As already noted, Wagner detected a slight acceleration of N_2O decomposition at 625° with the solution of Ga_2O_3 in ZnO. Schwab and Block obtained contradictory results. Hauffe and Schlosser attempted to explain the effect of the solution of lithium oxide in this case by assuming that outside the boundary layer there is reversal of electron conductivity to hole conductivity, which is intensified with a fall in the Fermi level. The artificiality and lack of foundation for this hypothesis is obvious. The similarity in the rules for the change in chemisorption of gas-acceptors of electrons and the decomposition of N_2O when Li_2O is dissolved in NiO make the explanation that the observed rules are the result of the change in the rate of N_2O adsorption more probable.

Exchange of hydrogen and deuterium. This catalytic process was investigated on ZnO and its solid solutions by Molinari and Parravano [9] and then by Heckelsberg, Clark, and Bailey [8]. In these two investigations it was observed that the solution of lithium oxide in ZnO reduces the catalytic activity of ZnO with respect to the exchange of hydrogen and deuterium. Solution of trivalent metal oxides Al_2O_3 and Cr_2O_3 increased it.

The effect of the solution of lithium oxide was explained by Hauffe [15] as the result of slowing of the desorption stage, which requires free electrons. It is assumed that the rate of hydrogen and D_2 adsorption is high and cannot be the stage determining the exchange rate. According to the data of Chizhikova and the author, the effect of the solution on the adsorption of gas-donors of electrons on ZnO makes such an explanation incorrect. The rate of adsorption of CO, a gas-donor of electrons, falls strongly with the solution of lithium oxide and it practically ceases at an Li content of 0.5 at. % as has been shown, gases belonging to the same group with respect to the direction of electron transfer, obey similar rules. For this reason the adsorption of hydrogen should be slowed with the solution of Li_2O in ZnO in analogy with the adsorption of CO. A fall in the adsorption rate should lead to a fall in the exchange rate.

SUMMARY

A comparison of the change in the rules of chemisorption of gas-acceptors and donors of electrons with catalytic activity for processes with gases of the same type showed that the change in the catalytic properties

of NiO and ZnO and their solid solutions may be explained by the effect of dissolved oxides Li_2O, Ga_2O_3, Fe_2O_3, etc.,on chemisorption. The change in chemisorption is considered to be connected with the effect of cations with an anomalous charge in the lattice points on the statistics of the active centers on the surface.

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KINETIC DETERMINATION OF THE ENERGIES OF BONDS FORMED
BY H, C, AND O ATOMS WITH A V_2O_3 CATALYST

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For developing the scientific bases of the selection of catalysts, it is necessary to accumulate data on the energies of bonds formed by the reacting atoms with atoms of the catalyst. According to the kinetic method developed by one of the authors [1], it is necessary to know the activation energies of several reactions on the same catalyst for determining the values of these bond energies. In the present work we carried out a kinetic investigation of the dehydrogenation of hydrocarbons and also the dehydrogenation and dehydration of alcohols over vanadium oxides in order to explore the possibilities of determining the energies of the bonds of H, C, and O with these catalysts. The work was one of a series of investigations carried out by the authors to compare the catalytic properties of vanadium, niobium, and tantalum oxides.

Vanadium, in the form of its oxides, is one of the commonest catalysts. Vanadium pentoxide is known largely as an oxidation catalyst [2]. Reports are encountered more rarely on the use of vanadium oxides as catalysts for the dehydrogenation of solid and liquid paraffins and oils [3], hydrogenation of naphthalene [4], and dehydrogenation of cyclohexane [5]. Catalysts containing vanadium oxides produce aromatization of paraffins [6-8]. In order to investigate the aromatizing properties of a vanadium oxide catalyst deposited on Al_2O_3, Plate and his co-workers [9] made a detailed study of the behavior of n-heptane [10], and also cyclopentane [11] and cyclohexane hydrocarbons [12] on this catalyst. In all cases the apparent activation energy ϵ was determined. The dehydrogenation of cyclohexane did not proceed smoothly and for the over-all process ϵ = 38.9 kcal/mole. Taylor and Yeddanapalli [13] also dehydrogenated cyclohexane over a vanadium oxide catalyst and found for various samples ϵ = 25-30 kcal/mole. Vanadium pentoxide has both a dehydrogenating and a dehydrating action on alcohols [14, 15]; it is interesting to note that paraffins with the same number of carbon atoms as the starting alcohols were formed at the same time [15]. The proportion of dehydrogenation and dehydration varied, depending on the method of preparing the catalyst.

Preliminary treatment of V_2O_5 with hydrogen increased the dehydrogenating capacity of the catalyst with respect to both hydrocarbons and alcohols [5, 6, 16, 17]; this method of preparing the V_2O_5 and its preliminary firing before treatment with hydrogen also affected the activity of the reduced samples [16]. As will be shown below, as the vanadium pentoxide was reduced, the catalyst acquired the capacity to produce the dehydrogenation of hydrocarbons practically without side reactions so that it became possible to determine the activation energy of the reaction.

EXPERIMENTAL

As a catalyst for the dehydrogenation of hydrocarbons and the dehydrogenation and dehydration of alcohols, we first investigated vanadium pentoxide prepared in the following way: chemically pure ammonium vanadate was fired in a porcelain dish at 400° for 2 hr until yellow, powdered V_2O_5 was obtained. Part of the powder was mixed with a small amount of distilled water and the mass obtained used to form small pyramids (3-5 mm),
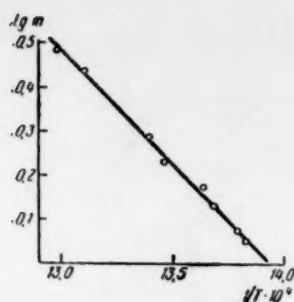
Fig. 1. Dehydrogenation of cyclohexane over V_2O_3. $\epsilon = 23,800$ cal/mole.

which were dried in a drying cupboard at 110° for 3 hr. In each case, 6 ml (bulk volume) of the catalyst prepared in this way was used.

The experiments were carried out in a flow catalytic apparatus (tube diameter 17 mm), fitted with a device for the automatic input of liquid at a constant rate and a eudiometer for measuring (at atmospheric pressure) the volume of gases liberated as a result of the reaction. All gas volumes were corrected to n.p.t. The temperature was measured with an accuracy of ±0.5° with a chromel—alumel thermocouple in a quartz picket in the center of the catalyst bed. In all experiments the liquid input rate was 0.15 ml/min.

Preliminary experiments with cyclohexane [b. p. 80.7° (755 mm) $n^{20}D$ 1.4265] and n-heptane [b. p. 98.3° (760 mm) $n^{20}D$ 1.3875] over vanadium pentoxide in the temperature range 450-500° both in an air atmosphere and in a nitrogen atmosphere (i.e., after preliminary flushing of the system with these gases) showed that these hydrocarbons were dehydrogenated very slightly over V_2O_5. The small amount of gas liberated (3.0-4.0 ml/min) contained, in the case of cyclohexane (in an air atmosphere), up to 25% of saturated hydrocarbons even at 470° and the remainder was practically hydrogen, while the amount of CO, CO_2, and unsaturated hydrocarbons varied over the range 0.3-0.7%; in the case of n-heptane, in contrast to cyclohexane, the gas contained up to 33.5% of unsaturated hydrocarbons, 36% of saturated hydrocarbons, a large amount of CO and CO_2 (20-32%), and 7-8% of hydrogen. n-Heptane also underwent cracking in a nitrogen atmosphere. At 465° the gas consisted of 50% saturated and 25% unsaturated hydrocarbons, and 24% hydrogen. With an increase in temperature, the amount of hydrogen in the gas increased due to dehydrogenation of the saturated hydrocarbons. Thus, at 520° the gas contained 27% of saturated hydrocarbons, 35% of hydrogen, 41.5% of unsaturated hydrocarbons, and 0.7-0.8% of CO and CO_2. It should be noted that the dehydrogenation of cyclohexane and n-heptane over V_2O_5 was accompanied by reduction of the latter (partly to V_2O_3).

In view of all that has been said, this catalyst did not satisfy the essential requirements and the results could not be used for accurate determination of the activation energies of the dehydrogenation of these compounds. We therefore carried out a more detailed investigation of the action of hydrogen-treated vanadium pentoxide, obtained by the method described above. The best results were obtained in the investigation of a catalyst reduced at 416-147° with dry, oxygen-free, electrolytic hydrogen for 7 hr in a flow catalytic apparatus. According to x-ray analysis, V_2O_3 was obtained by this reduction.

Cyclohexane was dehydrogenated over V_2O_3 in low yield (see below), but the reaction was not accompanied by appreciable decomposition processes. In experiments at 450° the gas consisted of 99.3% H_2 and 0.5% saturated hydrocarbons; a rise in temperature changed the gas composition very slightly and at 498° the gas contained up to 97% H_2, 2% saturated and 0.2-0.3% unsaturated hydrocarbons. As will be reported later, catalyst samples reduced completely to V_2O_3 gave different results. Therefore, as the main catalyst for the investigation we used V_2O_3 prepared by the method described above (sample 1).

Dehydrogenation of cyclohexane over V_2O_3 (sample 1) was carried out under the conditions described above over the temperature range 450-500°. The amount of gas liberated was measured over a period of 25-30 min, 10-12 min after the beginning of the experiment when a stationary state had been established. After 30-50 min operation, depending on the experiment temperature, the activity of the catalyst gradually fell (the activity was retained for a longer time at 450°) and it was not restored either by prolonged regeneration of the catalyst with hydrogen (up to 10 hr) at the experiment temperature and at a higher temperature or by oxidation of the carbonaceous film with air with subsequent reduction of the catalyst at the appropriate temperature. The activity was stabilized somewhat without being affected quantitatively if the experiments were carried out in a nitrogen atmosphere after preliminary flushing of the system with dry, purified nitrogen. However, the catalyst lost its activity even in this case and it was not restored by regeneration. Therefore a fresh portion of catalyst was used for each experiment in most cases and its original activity was checked at 450°. In experiments in a nitrogen atmosphere, at some temperatures investigated it was possible to confirm the constancy of the activity at 450° after operation (experiments 50, 51, 51, and 53, Table 1).

TABLE 1

Dehydrogenation of Cyclohexane Over V_2O_3. Catalyst Volume 6 ml, Cyclohexane Input rate 0.15 ml/min, mean log k_0 6.477, ϵ = 23,800 cal/mole

Experiment No.	Experiment temperature in °C	$\overline{m}$ in ml/min, n.p.t.	$\overline{m}$ in ml/min·ml of catalyst	m calculated from ϵ and the mean lg k_0	$\dfrac{\epsilon}{\lg k_\circ}\cdot 10^{-3}$	Degree of conversion in %
33*	450	1,16	0,193	0,186	3,67	3,7
60*	450	1,06	0,176	0,186	3,69	3,4
50*	450	1,13	0,186	0,186	3,68	3,6
57*	450	1,13	0,186	0,190	3,68	3,6
40	451	1,16	0,193	0,193	3,67	3,7
53	452	1,20	0,200	0,193	3,67	3,9
41	458	1,36	0,226	0,230	3,67	4,4
51	460	1,50	0,250	0,230	3,66	4,9
76	470	1,70	0,283	0,290	3,68	5,5
52	473	1,93	0,320	0,310	3,68	6,2
21	490	2,73	0,453	0,440	3,68	8,8
75	496	3,00	0,500	0,500	3,67	9,7
70	498	3,06	0,510	0,510	3,67	9,9

*Control experiments confirming the constancy of the catalyst activity during the series of experiments.
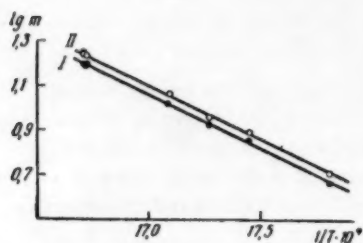
Fig. 2. Dehydrogenation (I) and dehydration (II) of isopropyl alcohol over V_2O_3; 1) ϵ = 20,600 cal/mole; 2) ϵ = 20,900 cal/mole.

The results of dehydrogenation of cyclohexane are given in Table 1 and Fig. 1. The numbers of the experiments in this and subsequent tables correspond to the sequence in which they were carried out. The value $\underline{m}$ is the amount of H_2 liberated in ml/min (allowing for the results of gas analysis) divided by 3, as 1 mole of cyclohexane liberates 3 moles of H_2. The data obtained were used to determine the activation energy of cyclohexane dehydrogenation over V_2O_3, the reaction constant, and the value $\epsilon/\log k_0$; the value obtained for the latter indicated a doublet mechanism for the reaction.

Conversion of isopropyl alcohol. Experiments with isopropyl alcohol were carried out in the temperature range 290-350° over fresh portions of catalyst (sample 1), which was not prepared in one batch. The results are given in Table 2. Experiments over different portions of catalyst in this and subsequent tables are separated by a line. Table 2 shows that the alcohol was dehydrogenated and dehydrated at all the temperatures investigated. The gas also contained up to 80-83% of saturated hydrocarbons. The latter could have been formed both as a result of decomposition processes and by secondary hydrogenation of unsaturated hydrocarbons from dehydration of the alcohol by hydrogen obtained by dehydrogenation of the alcohol. Analysis of the saturated hydrocarbons showed that they consisted almost solely of propane (up to 98.8-99.5%) and the unsaturated ones were propylene, indicating a secondary reaction. Analogous data were obtained by Komarevskii with alcohols over V_2O_5 [15]; he showed later [18] that unsaturated hydrocarbons are hydrogenated over a vanadium oxide catalyst. Therefore, it seemed possible to us to calculate the amounts of propylene and hydrogen formed by the primary reaction from the percentage of propane in the gas and add these to the amounts of propylene and hydrogen remaining in the gas to give the total amounts. Thus it was possible to calculate the degree of conversion of alcohol by dehydrogenation and dehydration separately. The amount of acetone in the catalyzate corresponded to the percentage of dehydrogenation of the alcohol calculated from the amount of hydrogen determined by the method given above. Thus, in experiments 14 and 15 (Table 2), the degree of dehydrogenation calculated from H_2 was 19.40 and 24.50%, respectively, and the values calculated from the acetone in the catalyzate were 19.35 and 24.00%.

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TABLE 2

Conversion of Isopropyl Alcohol Over V_2O_3. Catalyst Volume 6 ml, Alcohol Input Rate 0.15 ml/min

Experiment No.	Experiment temperature in °C	Dehydration of alcohol						Dehydrogenation of alcohol					Gas analysis in %				
		$m_{C_nH_{2n}}$ in ml/min	in ml/min, n.p.t.	$m_{C_nH_{2n}}$ ml/min·ml of catalyst	$m_{C_nH_{2n}}$ calc. from ε and mean lg k_0	$\frac{\varepsilon}{\lg k_0}\cdot10^{-1}$	degree of conversion in %	m_{H_2} in ml/min	m_{H_2} in ml/min·ml of catalyst	m_{H_2} calc. from ε and mean lg k_0	$\frac{\varepsilon}{\lg k_0}\cdot10^{-1}$	degree of conversion in %	H_2	C_nH_{2n}	CO	CO_2	C_nH_{2n+2}
2	302	6,4	6,1	1,02	1,02	2,62	13,9	5,6	0,93	0,94	2,64	12,8	4,0	12,0	0,2	0,6	83,5
5	326	13,6	12,8	2,13	2,13	2,62	29,2	11,8	1,96	1,95	2,64	27,0	4,3	12,0	0,5	0,5	82,5
1	327	14,0	13,2	2,20	2,19	2,62	30,2	12,1	2,01	2,01	2,64	27,7	3,8	11,7	0,3	0,6	83,0
3	349	16,9	15,6	2,60	—*	—	35,7	14,4	2,40	—*	—	32,9	5,5	13,6	0,4	0,4	80,1
4	360	19,9	18,5	3,08	—*	—	42,3	16,4	2,73	—*	—	37,5	3,4	14,2	0,3	0,8	79,1
6	379	22,0	20,1	3,35	—*	—	46,0	17,2	2,83	—*	—	39,3	7,9	21,2	0,8	0,3	70,3
Mean				lg k_0 = 7,963**; ε = 20 900 cal/mole***						Mean lg k_0 = 7,924**; ε = 20 900 cal/mole**							
11	288	5,4	5,15	0,86	0,89	2,59	11,7	4,9	0,82	0,82	2,59	11,2	3,2	8,5	0,7	0,2	86,5
12	300	8,2	7,85	1,31	1,28	2,58	17,9	7,3	1,21	1,21	2,59	16,9	3,0	8,9	0,6	—	86,5
14	306	9,5	9,06	1,51	1,56	2,59	20,7	8,5	1,42	1,45	2,59	19,4	3,8	10,2	0,6	—	85,3
15	312	12,1	11,56	1,93	1,87	2,58	26,4	10,7	1,78	1,75	2,59	24,5	4,0	11,1	—	—	84,4
10	325***	17,7	16,97					15,5					4,2	12,4	0,7	—	83,0
13	325***	17,5	16,63					15,3					4,2	12,1	0,8	—	83,0
16	325***	17,9	17,02	2,83	2,79	2,58	38,8	15,5	2,60	2,58	2,59	35,7	4,2	12,6	0,7	—	82,5
Mean				lg k_0 = 8,090; ε = 20 900 cal/mole						Mean lg k_0 = 7,948; ε = 20 600 cal/mole							
19	288	3,5	3,3	0,55	—	2,64	7,6	3,2	0,53	—	2,65	7,3	5,0	8,3	0,2	0,2	86,0
20	325	11,3	10,6	1,77	—	2,64	24,2	9,8	1,63	—	2,64	22,4	5,4	12,2	0,2	—	81,5
				lg k_0 = 7,893; ε = 20 900 cal/mole						lg k_0 = 7,698; ε = 20 500 cal/mole							

* Not calculated (see text).

** From experiments 1, 2, and 5.

*** Experiments to check the constancy of the catalyst activity.

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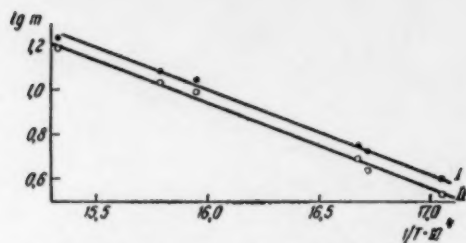
Fig. 3. Dehydrogenation (I) and dehydration (II) of ethyl alcohol over V_2O_3: I and II ϵ = = 19,500 cal/mole.

Table 2 gives the total amount of propylene and hydrogen formed in the reaction, determined by the method given above. This table shows that the dehydrogenation and dehydration of isopropyl alcohol over V_2O_3 above 327° give high yields (experiments 3, 4, and 6); this made it impossible to calculate the activation energies accurately by using log $\underline{m}$ (where $\underline{m}$ is the amount of gas liberated in ml/min) instead of log $\underline{k}$ in the Arrhenius equation. However, the activation energies could be calculated from the results of determinations in experiments 1, 2, and 5, where the degree of conversion did not exceed 30%. The activation energies of dehydration and dehydrogenation of isopropyl alcohol over V_2O_3 were found to be the same and equaled 20.9 kcal/ /mole. As the determination of an activation energy from three experiments may be inaccurate, we carried out a whole series of experiments with isopropyl alcohol in the range 288-327° over fresh portions of catalyst sample 1. The results are given in the middle section of Table 2 and in Fig. 2. The activation energies for dehydrogenation and dehydration of the alcohol in this case were also practically identical with each other and with the activation energies determined in previous experiments. The somewhat large amounts of gas liberated in ml/min are apparently explained by a certain small change in the duration of firing of V_2O_5 during its preparation which, according to reports in [16] affects the subsequent activity of the reduced sample. The latter circumstance may also explain the somewhat lower activity of another portion of V_2O_5 (experiments 19 and 20, Table 2). However, this has no effect on the value of the activation energy. The activation energies for the dehydrogenation and dehydration of isopropyl alcohol over V_2O_3 obtained in this way were practically identical and equaled on an average 20.9 and 20.6 kcal/mole.

It may also be considered that the formation of unsaturated hydrocarbons over V_2O_3 occurs as a result of direct reduction of alcohol by hydrogen formed during dehydrogenation as was considered in the work of Stoddart and Kemball [19] on the hydrogenation of acetone over platinum. In the case of this second mechanism, the total amount of hydrogen formed in the reaction is also found from the sum of hydrogen and saturated hydrocarbons in the gas mixture (as 1 mole of hydrogen is consumed per mole of alcohol in the formation of saturated hydrocarbons by reduction of alcohol), which will also correspond to the amount of acetone in the catalyzate, while the amount of propylene characterizing the dehydrating capacity of the oxide will correspond only to the amount of propylene present in the gas mixture. In this case the dehydration activation energy equals 27.5 kcal/ /mole; at the same time the activation energy for dehydrogenation of the alcohol is unchanged. The activation energies were calculated as in the case of the first mechanism (see Table 2) and the calculations are not given here to save space.

It should be noted that in experiments with isopropyl alcohol the catalyst retained its activity much longer than in experiments with cyclohexane without any regeneration. It was therefore possible to carry out experiments with the same portion of catalyst at several temperatures, returning several times to the original temperature (325°) to check the initial activity. The initial activity of a fresh sample was also checked on cyclohexane at 450°. However, a catalyst that had partly lost its activity in a reaction with alcohol could not be regenerated as was also the case in experiments with cyclohexane. In addition, if after alcohol we introduced cyclohexane, which requires a higher temperature for its dehydrogenation, the catalyst activity fell more rapidly. It is interesting that according to x-ray diffraction patterns, a catalyst that had partially lost its activity was V_2O_3, but in a more disperse state than before the experiments.

Conversion of ethyl alcohol over V_2O_3. An investigation analogous to that described above was also carried out with ethyl alcohol over V_2O_3 (sample 1). In this case the experimental temperatures were somewhat higher and lay within the ranges of 325-375° and 313-379°. As in the reaction with isopropyl alcohol, together with hydrogen and unsaturated hydrocarbons (ethylene), the reaction with ethyl alcohol yielded a large amount of saturated hydrocarbons which, according to analysis, consisted almost all of ethane. The amounts of hydrogen and ethylene formed as a result of the reaction were calculated as described above, considering firstly the first mechanism for the formation of saturated hydrocarbons, i.e., by hydrogenation of ethylene. As the results, which are given in Table 3 and Fig. 3, show, the activation energies for dehydration and dehydrogenation of ethyl alco-

TABLE 3

Conversion of Ethyl Alcohol Over V_2O_3. Catalyst Volume 6 ml; Alcohol Input Rate 0,15 ml/min

Experiment No.	Experiment temperature in °C	V of gas liberated in ml/ml a,p,t.	Dehydration of alcohol					Dehydrogenation of alcohol					Gas analysis in %				
			$m_{C_nH_{2n}}$ in ml/min	$m'_{C_nH_{2n}}$ in ml/min · ml of catalyst	$m_{C_nH_{2n}}$ calc., from ε and mean lg k_0	$\frac{\varepsilon}{\lg k_0}$ · 10^{-3}	degree of conversion	m_{H_2} in ml/min	m_{H_2} in ml/min · ml of catalyst	m_{H_2} calc., from ε and mean lg k_0	$\frac{\varepsilon}{\lg k_0}$ · 10^{-3}	degree of conversion	CO_2	C_nH_{2n}	CO	H_2	C_nH_{2n+2}
80	326	4,7	3,8	0,63	—	2,81	6,6	4,5	0,75	—	2,79	7,8	0,4	2,3	0,9	16,7	79,2
84	375	16,5	13,6	2,27	—	2,81	23,8	15,8	2,63	—	2,79	27,6	0,5	3,3	1,0	16,6	79,5
85	326*	4,8	4,1	—	—	—	6,7	4,7	—	—	—	8,0	0,4	1,8	—	14,2	84,1
			lg k_0=7,142;			ε = 20 100 cal/mole		lg k_0 = 7,107;			ε = 19 800 cal/mole						
88	313	4,2	3,4	0,57	0,54	2,77	5,9	3,9	0,65	0,62	2,74	6,7	1,4	1,8	1,6	16,5	78,7
87	325	5,5	4,4	0,73	0,69	2,77	7,6	5,3	0,88	0,79	2,74	9,2	—	1,8	2,6	17,1	78,8
93	326*	6,0	4,9	—	—	—	8,4	5,7	—	—	—	9,9	0,6	2,3	1,2	15,8	79,7
94	336	8,9	6,9	—	—	—	—	8,1	—	—	—	—	Her	2,9	4,6	13,7	77,5
89	354	12,0	9,9	1,65	1,57	2,77	17,2	11,1	1,85	1,80	2,75	19,3	1,4	3,2	2,0	13,6	79,2
90	360	13,2	10,8	1,80	1,86	2,79	18,7	12,1	2,01	2,14	2,77	21,0	1,0	3,2	3,9	13,0	79,0
92	379	18,9	15,5	2,68	2,93	2,80	26,9	17,2	2,87	2,69	2,78	29,9	1,1	3,2	4,5	12,2	78,7
		Mean	lg k_0=7,011;			ε = 19 500 cal/mole		Mean	lg k_0=7,070;			ε = 19 500 cal/mole					

* Experiments to check the constancy of the catalyst activity during the series of experiments.

TABLE 4

Conversion of Isopropyl Alcohol Over V_2O_3 Containing Higher Oxides of Vanadium. Catalyst Volume 6 ml, Alcohol Input Rate 0,15 ml/min

Experiment No.	Experiment temperature in °C	Dehydration of alcohol					Gas analysis in %					Catalyst composition according to x-ray analysis data
		V of gas liberated in ml/min n.p.t.	Dehydration of alcohol, mC_nH_{2n} in ml/min	mH_2 in ml/min	mH_2 in ml/min calc. on acetone	amount of acetone in catalyzate in %	CO_2	C_nH_{2n}	CO	H_2	C_nH_{2n-2}	
101	301	9,5	9,5	6,6	—	—	0,4	25,7	0,4	3,5	69,6	V_2O_3 plus higher oxides of vanadium (sample 2)
102	313	14,0	13,4	ε_1{ 9,7	—	—	0,6	27,1	0,9	3,7	66,8	
100	325	18,6	—		—	—	—	—	—	—	—	
103	325	19,0	17,9	13,2	—	—	1,0	28,9	0,3	4,2	65,5	
104	288	3,4	3,2	2,3	—	—	Her	30,1	1,0	4,2	65,3	V_2O_3 plus higher oxides of vanadium (sample 3)
105	325	12,0	11,3	ε_1{ 6,8	—	—	0,2	41,8	0,8	4,2	52,6	
109	290	—	—		4,4	9,95	—	—	—	—	—	Catalyst reduced to V_2O_3 during operation
107	300	7,2	6,84	5,3 ε_2	6,3	14,5	0,3	25,0	0,5	4,0	70,0	V_2O_3 plus higher oxides of vanadium (sample 4)
106	310	10,5	9,06	7,9	9,6	22,1	Her	23,7	0,6	5,0	71,2	V_2O_3 plus higher oxides of vanadium (sample 4)
105	325	15,9	15,10	10,9	13,1	30,1	0,3	28,5	2,8	2,0	66,5	
108	325	13,8	12,70	ε_1{ 11,5	—	—						V_2O_3
110	326	13,6			—	—	0,5	13,0	1,0	4,5	80,5	
111	326	14,0			—	—						
112	300	5,8	5,70	5,2	—	—	0,8	12,3	0,6	2,9	86,8	Catalyst reduced to V_2O_3 during operation

$\varepsilon_1 = 20\ 400$ cal/mole $\varepsilon_2 = 20\ 200$ cal/mole

hol over V_2O_3 were found to be identical (19.5 kcal/mole) and very close to the activation energies for the corresponding reactions of isopropyl alcohol over V_2O_3 (20.9 and 206 kcal/mole).

If it is assumed that the saturated hydrocarbons were formed according to the second mechanism (direct reduction of alcohol), then the value of ϵ for the dehydration of ethyl alcohol is increased to 26.8 kcal/mole, which is very close to the corresponding value of ϵ for isopropyl alcohol (27.5 kcal/mole).

Thus, depending on whether the calculation is carried out for the first or second mechanism, only the value of ϵ for dehydration changes and is the same for the two alcohols. The similarity of the values of ϵ for the two alcohols reconfirms the structural principles of the multiplet theory of catalysis, namely, the identical orientation of the molecules [20].

On the basis of the data obtained on the activation energies of the dehydrogenation and dehydration of alcohols and the dehydrogenation of cyclohexane it is possible to calculate the energy barriers of the reactions, $E = 4/3 \epsilon$, and the energies of the bonds of H, C, and O with the catalytically active centers of vanadium oxide (V_2O_3).

Calculation of bond energies. The calculation was carried out according to formula (1) and (2) in [21]. The energies of the bonds $C-H$, $C-O$, and $O-H$ were taken from Cottrell's monograph [22].

The energies of the bonds with the catalyst, Q, calculated from ϵ for the dehydrogenation of cyclohexane and the dehydrogenation and dehydration of isopropyl alcohol (I) and ethyl alcohol (II), respectively, were found to be as follows:

a) considering the first mechanism of the secondary reaction:

$$(I)\ Q_{HK} = 54.5;\ Q_{CK} = 20.6;\ Q_{OK} = 44.9\ \text{kcal/mole},$$

$$(II)\ Q_{HK} = 54.1;\ Q_{CK} = 20.6;\ Q_{OK} = 47.2\ \text{kcal/mole}$$

b) considering the second mechanism of the secondary reaction:

$$(I)\ Q_{HK} = 58.5;\ Q_{CK} = 16.2;\ Q_{OK} = 40.1\ \text{kcal/mole},$$

$$(II)\ Q_{HK} = 58.9;\ Q_{CK} = 15.7;\ Q_{OK} = 41.6\ \text{kcal/mole}$$

Reactions over vanadium oxide incompletely reduced to V_2O_3. All the results given above were obtained during the investigation of a catalyst formed as a result of complete reduction of V_2O_5 to V_2O_3 (sample I). In addition we also investigated the activity of catalyst samples which had not been reduced completely to V_2O_3 (samples 2, 3, and 4) and which, according to x-ray analysis, contained intermediate higher oxides of vanadium together with V_2O_3. The results of experiments with isopropyl alcohol over such catalysts are given in Table 4. As this table shows, the nature of the conversion of isopropyl alcohol remained largely the same; the gas liberated also contained a large amount of saturated hydrocarbons. However, in this case the gas contained considerably more unsaturated hydrocarbons and dehydration predominated over dehydrogenation (the calculation was carried out as described above for the first mechanism).

As the catalyst was reduced to V_2O_3 during the reaction due to hydrogen liberated in the reaction, a catalyst that had operated for some time had a lower activity with respect to dehydration and the results obtained were analogous to those for the conversion of isopropyl alcohol over V_2O_3 (see experiments 105, 110, 107, and 112 in Table 4). According to x-ray diffraction patterns, the catalyst was actually V_2O_3 after operation.

Determination of the acetone in the catalyzate made it possible to calculate the degree of dehydrogenation of alcohol and this was found to be close to the degree of dehydrogenation calculated from gas analysis data. The activation energies for dehydrogenation obtained from the same data were found to be practically identical (20.2 and 20.4 kcal/mole, respectively) and close to the values of ϵ for dehydrogenation of ethyl alcohol over V_2O_3 (19.5 kcal/mole).

The dehydrogenation of cyclohexane over incompletely reduced samples was accompanied by decomposition; in this case a very low content of higher oxides in the V_2O_3 resulted in the gas from cyclohexane dehydrogenation containing a considerably larger amount of saturated hydrocarbons (up to 15-22% in comparison with 1-3% over V_2O_3).

Laboratory worker Z. M. Skul'skaya played a large part in the experimental work. The x-ray structural analysis of the catalysts was carried out under the direction of R. P. Ozerov in the Scientific Research Institute of Fertilizers and Insectofungicides and the authors would like to express their sincere thanks to him for this. The authors would also like to thank G. V. Isagulyants for participating in the discussion of the results.

SUMMARY

1. An investigation was made of the activity of vanadium oxides in the dehydrogenation of cyclohexane, and the dehydrogenation and dehydration of ethyl and isopropyl alcohols. It was found that the relative dehydrogenating and hydrogenating capacity of vanadium oxides increases in the case of both alcohols and hydrocarbons as they are reduced to V_2O_3, and is maximal for V_2O_3. Corresponding samples were investigated by x-ray diffraction methods.

2. Over the temperature range 450-500°, vanadium trioxide produces dehydrogenation of cyclohexane with up to 10% conversion and, in contrast to vanadium pentoxide, it produces hardly any side processes (the gas consists of 97-99% H_2). The activation energy of this reaction was determined.

3. Vanadium trioxide has a dehydrogenating and a dehydrating action on alcohols and there is a secondary reaction with the hydrogen formed. The activation energies for the dehydrogenation and dehydration of ethyl and isopropyl alcohols were calculated, considering two possible mechanisms for this secondary reaction.

The activation energies for the reactions of the two alcohols were found to be similar, which is in agreement with the multiplet theory of catalysis.

4. The energies of the bonds of H, C, and O atoms with the catalytically active centers of vanadium trioxide were determined.

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CATALYTIC ALKYLATION OF ISOBUTANE WITH ETHYLENE
UNDER PRESSURE AT HIGH TEMPERATURES

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The reaction of isobutane with ethylene in the presence of such catalysts as aluminum chloride [1] or hydrogen fluoride with boron trifluoride added [2] forms an alkylate, the hexane fraction of which consists mainly of 2,3-dimethylbutane. The yield of hexane fraction represents ~45% of the liquid product. In contrast to this, the thermal alkylation [3] of isobutane with ethylene under pressure (510°, 315 atm) forms an alkylate whose hexane fraction consists mainly (80%) of 2,2-dimethylbutane; 20% of 2-methylpentane is formed simultaneously. The yield of the hexane fraction is ~30%. Thus, under these conditions ethylene adds largely to the tertiary C atom of isobutane to form 2,2-dimethylbutane

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{CH}} + CH_2=CH_2 \rightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CH_3,$$
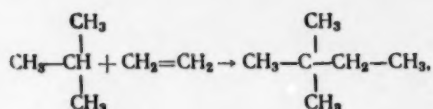
and to a lesser extent to a primary C atom:

$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_3 + CH_2=CH_2 \rightarrow CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_2-CH_3.$$
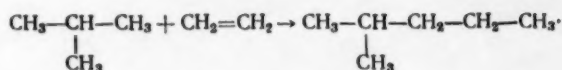
In high-temperature alkylation (427°, 200 atm) in the presence of a homogeneous catalyst, namely 1-3% of chloro or nitro derivatives of naphthalene [4], the main component of the hexane fraction is also 2,2-dimethylbutane. The yield of hexane fraction is 43%. The reaction of n-butane with ethylene under the same conditions forms 3-methylpentane, i.e., the product of addition to the secondary C atom:

$$\underset{\underset{CH_3}{\overset{|}{\underset{|}{CH_2}}}}{\overset{\overset{CH_3}{|}}{CH_2}} + CH_2=CH \rightarrow \underset{\underset{CH_3}{\overset{|}{\underset{|}{CH_2}}}}{\overset{\overset{CH_2}{|}}{CH_2}}-CH_2-CH_3$$
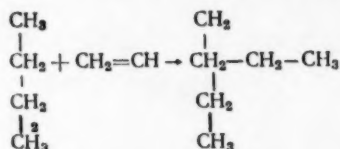
in almost half the yield (28%). As we showed [5-8], the addition of an olefin to a normal paraffin in the presence of solid catalysts (aluminum oxide or aluminosilicate) at high temperatures and pressures (450°, 300-500 atm) occurs predominantly at the C atom in position 2, for example:

$$CH_3-CH_2-CH_2-CH_2-CH_3 + CH_2=CH-CH_3 \rightarrow CH_3-CH_2-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_2-CH_3.$$
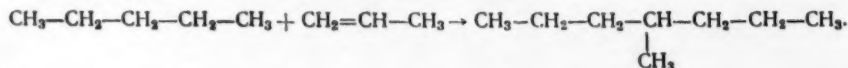
In the present work we studied the alkylation of isobutane in the presence of aluminum oxide catalyst at high temperature under pressure. The data obtained show that under these conditions ethylene and propylene react with isobutane predominantly at the tertiary and, to a lesser extent, at the primary carbon atom. It was also possible to isolate an octane fraction which was mainly the alkylation product of the 2,2-dimethylbutane formed. However, at this stage the alkylation occurred at the primary C atom of the unbranched end of the carbon chain:

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CH_3 \rightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CH_2-CH_2-CH_3.$$
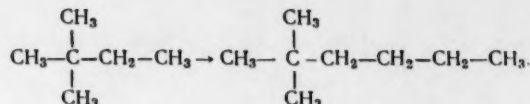
This fact confirmed the stepwise nature of the alkylation process which we established previously [8]. It should be noted that in the presence of sulfuric acid, for example, hydrocarbons with a quaternary C atom (neohexane and 2,2,4-trimethylpentane) do not react with olefins [9]. An octane fraction was also obtained in the thermal alkylation of isobutane with ethylene (9% of the alkylate weight), but its composition was not investigated.

It seemed interesting to compare the yields of the main product of primary alkylation obtained during the alkylation of n-butane and isobutane with ethylene under different experimental conditions. In the presence of aluminum oxide, the product of alkylation of n-butane with ethylene at the secondary C atom (2-methylpentane) was formed in higher yield (29 weight %) than the product from alkylation of isobutane with ethylene at the tertiary C atom, i.e., 2,2-dimethylbutane (20%). On the other hand, in the presence of homogeneous catalysts [4] the yields of the same products were 26 and 43%, respectively.

During thermal alkylation there was comparatively ready addition of olefin to secondary and tertiary C atoms of the paraffin in the reaction of propane and isobutane with ethylene [3]. It was found that under these conditions the yield of the primary product from alkylation at the tertiary carbon atom was greater than that at the secondary carbon atom.

EXPERIMENTAL

The experiments were carried out under flow conditions on the apparatus described previously [5]. The aluminum oxide catalyst used was prepared in the following way: aluminum oxide was impregnated with an aqueous solution of potassium bifluoride (10% of the weight of Al_2O_3) and fired in a stream of air at 400° until the hydrofluoric acid had been removed and was then treated twice with sulfuric acid (1:1) and washed to remove $SO_4^=$ [6].

The reaction was carried out with industrial isobutane fraction (81.2% isobutane, 12.4% n-butane, and 6.4% propane) and with ethylene containing 8.7% of ethane. The alkylates obtained in the experiments were freed from isobutane and fractionated on a column with an efficiency of 70 theoretical plates. The content of unsaturateds in the alkylate fractions was determined by the bromine method [10]. Individual narrow fractions were separated from unsaturateds by chromatography on silica gel and then analyzed by Raman spectroscopy. *

Table 1 gives the experimental conditions, the degree of conversion of ethylene, and the yields of alkylates. This table shows that at 450° the alkylation may be accomplished even at a pressure of 300 atm. With a rise in pressure from 300 to 500 atm (experiments 3 and 4), the alkylate yield rose from 63 to 110%, calculated on the ethylene taken for the reaction. With a rise in the ethylene content of the mixture, the alkylate yield increased (experiments 1-3). The alkylate from experiment 2 was found to contain 24% of hexane fraction (b. p. 47-70°); half of it distilled over the range 48-49°.

Table 2 gives the characteristics of individual fractions of the alkylates obtained in experiments 2 and 4. Figure 1 shows the fractionation curve of the catalyzate from experiment 4. The curve clearly shows three horizontal sections corresponding to the boiling points of the three alkylation products formed. In the alkylate of experiment 4, which was carried out at 500 atm, the content of hexane fraction represented 33% of the catalyzate; 60% of this distilled over the range 48-49°.

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* The Raman spectral analyses of the fractions were carried out by Yu. P. Egorov and G. K. Gaivoronskaya.

TABLE 1

Experiment No.	Temperature in °C	Pressure in atm	Ethylene content of mixture in weight %	Experiment duration in min	Space velocity	Degree of conversion of ethylene in %	Alkylate yield in weight %	
							on ethylene passed	on products collected
1	450	300	12,4	240	1400	66	59	7,3
2	450	300	15,0	330	1350	74	71	10,7
3	450	500	10,2	165	1350	55	63	10,2
4	450	500	10,2	320	1350	72	110	11,2

* In liters of gas per liter of catalyst per hr.

TABLE 2

B. p. of fraction in °C	Experiment 2 at 300 atm			Experiment 4 at 500 atm		
	amount in weight %	n_D^{20}	bromine number	amount in weight %	d_4^{20}	bromine number
26,3 – 47	4,3	1,3680	53	3,6	1,3652	40
47 —52	11,5	1,3681	6	20,0	1,3672	7
52 —57	1,1	1,3710	25	1,0	1,3697	21
57 —62	6,4	1,3756	17	7,4	1,3723	16
62 —70	5,3	1,3890	90	4,8	1,3849	73
70 —100	9,2	1,3965	69	8,3	1,3967	59
100 — 106	10,5	1,3962	13	11,8	1,3945	9
Residue	51,7	—	—	43,7	—	—
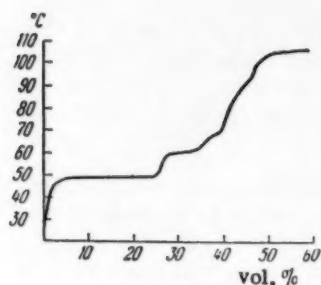
Fig. 1.

The fraction freed from unsaturateds had $n^{20}D$ 1.3673; d^{20}_4 0.6491 and the Raman spectral frequencies (in cm^{-1}): 346 (0), 361 (0), 415 (1), 493 (1), 712 (10), 880 (4), 939 (6), 1018 (1), 1076 (1), 1230 (4 broad), 1264 (5), 1318 (1), 1449 (3), 1464 (6). These properties correspond to 2,2-dimethylbutane.

In addition to neohexane, the fraction also yielded ~25% of 2-methylpentane with b. p. 59.6-61.8°; $n^{20}D$ 1.3715; d^{20}_4 0.6549. and the Raman spectral frequencies (in cm^{-1}): 322 (3 broad), 385 (0), 449 (7), 792 (0), 823 (9), 961 (0), 891 (3 broad), 994 (0), 957 (5), 1010 (1), 1045 (7), 1068 (1), 1103 (4), 1146 (6), 1172 (3), 1199 (1), 1240 (0), 1300 (5 broad), 1341 (4), 1362 (0), 1386 (1), 1451 (10), 1466 (10).

In addition to the hexane fraction, the fractionation also yielded an octane fraction with b. p. 105-106.5° (10-11 weight %); after removal of the unsaturateds it had $n^{20}D$ 1.3940; d^{20}_4 0.6968 and Raman spectral frequencies (in cm^{-1}): 307 (5), 498 (2), 737 (1), 753 (8), 873 (2), 894 (3), 911 (5), 933 (7), 1015 (0), 1060 (5), 1089 (0), 1101 (5), 1141 (1 broad), 1197 (7 broad), 1315 (5), 1389 (1), 1450 (9), 1469 (8). These properties correspond to 2,2-dimethylhexane.

Propylene also reacted with isobutane at the tertiary carbon atom in the presence of the aluminum oxide catalyst [11]. In this experiment we used an industrial fraction containing 81.2% of isobutane, 12.4% of n-butane, and 6.4% of propane. The propylene concentration in the reaction mixture was 16.5 weight %. An experiment at 450° and 500 atm gave an alkylate in 70% yield, calculated on the propylene passed. The bromine number of the alkylate was 66. The heptane fraction of the alkylate (70-100°) represented 24 weight % and had $n^{20}D$ 0.6928 and d^{20}_4 1.3894; ~40% of it (9.7 weight % of the alkylate) distilled over the narrow range of 77-82°. Judging by the boiling point, this fraction contained 2,2-dimethylheptane, i.e., the product from addition of the propylene to the tertiary atom of isobutane. The alkylate obtained from n-butane and propylene

under the same conditions yielded 22% of a fraction with b. p. 89-92°, containing 3-methylhexane, i.e., the product from addition of propylene at the secondary C atom of n-butane.

Thus, in contrast to homogeneous catalysts, with an aluminum oxide catalyst the alkylation by propylene at the tertiary C atom of isobutane proceeds with somewhat more difficulty than at the secondary C atom of n-butane.

SUMMARY

1. In the presence of aluminum oxide at elevated temperature and pressure, ethylene reacts with isobutane predominantly at the tertiary C atom and, to a lesser extent, at the primary C atom. 2,2-Dimethylbutane and 2-methylpentane are thus formed.

2. Neohexane obtained in the reaction also reacts with ethylene to form 2,2-dimethylhexane, indicating the stepwise nature of the alkylation process.

3. In the presence of an aluminum oxide catalyst, an olefin (ethylene and propylene) adds to the tertiary C atom of isobutane with more difficulty than to the secondary carbon atom of n-butane.

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*Original Russian pagination. See C. B. Translation.

PARTICIPATION OF SOLVENT IN THE ACTIVATED COMPLEX IN MENSHUTKIN REACTIONS

COMMUNICATION 1. KINETICS OF THE REACTION OF PYRIDINE WITH ETHYL IODIDE IN ETHANOL AT PRESSURES UP TO 2000 kg/cm²

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The problem of the role of the solvent in Menshutkin reactions has been discussed in the literature for several decades. In 1948 Swain and Eddy [1] came to the conclusion that these reactions proceed by a trimolecular mechanism and in addition to amine and alkyl halide molecules, one solvent molecule, solvating the halogen atom, also participates in the activated complex. However, this point of view is not generally accepted [2]. On the other hand, in recent years the opinion has frequently been put forward [3-5] that the activated complex in Menshutkin reactions is solvated to almost the same extent as ions of the reaction product.

To determine the solvation of the activated complex, it is possible to use data on the effect of pressure on the reaction rate [6]. In the case of dilute solutions, the pressure dependence of the rate constants of a bimolecular reaction makes it possible to find the change in volume of the system $\Delta v^{\neq}$ with formation of one mole of activated complex from reagent molecules from the equation:

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = -\left(\frac{\Delta v^{\neq}}{RT} + \varkappa\right). \tag{1}$$

Here k is the rate constant of the reaction; $\varkappa = -1/V\,(\partial V/\partial P)_T$, where V is the volume of solvent.

In a number of cases one expects a relation between the value of $\Delta v^{\neq}$ and the nature of the solvent. Let us assume, for example, that in a bimolecular reaction the molecules of the starting material are solvated to a greater extent than the activated complex. Then with the formation of the activated complex some of the solvent molecules pass from the solvation envelopes of the reagent molecules into the volume. This process must be accompanied by a certain increase in volume, as in the solvation envelopes the solvent molecules are packed more tightly than in the volume of the solvent itself. If the activated complex is more solvated than the starting molecules, then the volume effect caused by the transfer of solvent molecules into the solvation envelope of the activated complex will be negative. This phenomenon will naturally be reflected by the value of $\Delta v^{\neq}$.

In the present work we give the results of studying the kinetics of the reaction of pyridine with ethyl iodide

$$C_5H_5N + C_2H_5I \rightarrow C_5H_5NC_2H_5I$$
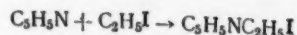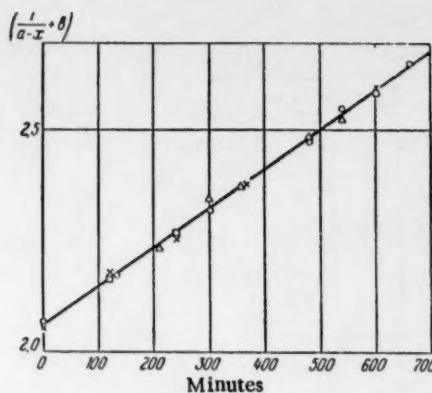
Fig. 1. Results of measuring the reaction rate constants at atmospheric pressure.

in ethanol at high pressures. In combination with the results of some other measurements (see communication 2), the data obtained make it possible to assess approximately the degree of solvation of the activated complex in the Menshutkin reaction studied. The effect of pressure on the rate constant of the reaction of pyridine with ethyl iodide in ethanol at 60° was studied previously [7]. The authors found that at this temperature the rate constant increased by a factor of 4.9 when the pressure was raised from atmospheric to 3000 kg/cm². Unfortunately, in the work cited the rate constants of the reaction were measured only at these two pressures. To calculate the value of $\Delta v^{\neq}$ from Eq. (1) it is necessary to construct a curve of the pressure dependence of the logarithm of the rate constant of the reaction at four pressures (from atmospheric to 2000 kg/cm²).

EXPERIMENTAL

The pyridine we used for the reaction was prepared by drying "pure" grade commercial product over KOH and distilling it on a fractionating column with an efficiency of 40 theoretical plates. A fraction with b. p. 115.5° (760 mm); d^{20}_4 0.9832 was collected for the investigation. The ethyl iodide was treated with sulfuric acid (3 vol. of H_2SO_4 : 1 vol. of pure H_2O) and then distilled; it had b. p. 72.2-72.4° (760 mm); d^{20}_4 1.9375. The ethyl alcohol was dried with CaO, distilled, finally dried over metallic Ca, and redistilled; it had b. p. 78.4°; d^{20}_4 0.7894; $n^{20}D$ 1.3614. The acetone was boiled with $KMnO_4$, distilled on a column, dried with potassium carbonate, and redistilled; it had b. p. 55.0° (730 mm); d^{20}_4 0.7912; $n^{20}D$ 1.3591.

Investigation of the kinetics of the reaction of pyridine with ethyl iodide in ethanol. The kinetic measurements were carried out in the apparatus described in [8] at 50 ± 0.1° and pressures of 1, 500, 1000, and 2000 kg/cm². Solutions of C_5H_5N and C_2H_5I (1 M), prepared in 100 ml flasks by dissolving samples of these substances in absolute ethanol, were rapidly mixed and part of the solution obtained poured into the high-pressure vessel, which was in a thermostat at the given temperature. A pressure was then produced rapidly in the vessel and the moment when the required pressure was reached was considered the beginning of the reaction. The initial pyridine concentration was determined in the remaining portion of solution. After definite time intervals, 10 ml samples were withdrawn from the vessel. In each experiment we removed 4-5 samples and the maximum degree of conversion was 0.20-0.35. The determination of the initial concentration of pyridine in the solution and the analysis of the samples taken during the reaction were carried out by a modification of the procedure described in [7]. A sample (10 ml) of the solution investigated (at 20°) was placed in a conical titration flask and 10 ml of alcohol added, followed by sufficient distilled water to give a total solution volume of 120 ml after titration. The pyridine was then titrated with 0.1 N HCl solution with Dimethyl yellow + Methylene blue as indicator. A blank sample (100 ml of water and 20 ml of alcohol) was titrated in parallel. Three to four experiments were carried out at each pressure. In all the experiments the initial concentrations of pyridine and ethyl iodide were ~0.5 M (at 20°). The rate constants were calculated from the equation:

$$k = \frac{1}{\tau} \left[\left(\frac{1}{a-x} - \frac{1}{a} \right) + \frac{a-b}{2} \left(\frac{1}{(a-x)^2} - \frac{1}{a^2} \right) + \frac{(a-b)^2}{3} \left(\frac{1}{(a-x)^3} - \frac{1}{a^3} \right) + \ldots \right], \qquad (2)$$

where a is the initial concentration of C_5H_5N, b is the initial concentration of C_2H_5I, and x is the concentration of $C_5H_5NC_2H_5I$ at moment τ.

Equation (2) was obtained by expanding into a series the expression obtained by integration of the equation for the rate of a bimolecular equation:

$$\frac{dx}{d\tau} = k(a-x)(b-x). \qquad (3)$$

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TABLE 1

Determination of Reaction Rate Constant at Atmospheric Pressure

Experiment 1 $a=0,5005;\ b=0,4984$			Experiment 2 $a=0,5017;\ b=0,5013$			Experiment 3 $a=0,5005;\ b=0,5007$			Experiment 4 $a=0,5017;\ b=0,5000$		
τ in min	x in mole/liter	$k\cdot10^4$ in liter·mole^{-1}·min^{-1}	τ in min	x in mole/liter	$k\cdot10^4$ in liter·mole^{-1}·min^{-1}	τ in min	x in mole/liter	$k\cdot10^4$ in liter·mole^{-1}·min^{-1}	τ in min	x in mole/liter	$k\cdot10^4$ in liter·mole^{-1}·min^{-1}
130	0,0249	8,34	210	0,0394	8,37	120	0,0230	8,28	240	0,0448	8,44
300	0,0546	8,46	360	0,0669	8,83	240	0,0436	8,21	365	0,0669	8,72
480	0,0826	8,53	480	0,0856	8,85	360	0,0650	8,57	480	0,0847	8,75
540	0,0941	8,89	540	0,0973	8,54	480	0,0841	8,69	600	0,1023	8,83
660	0,1089	8,74				600	0,1008	8,68			

Footnote: The values of k obtained in experiments in a steel reactor at atmospheric pressure agreed within the limits of measurement errors with the results of the determination of k in a glass vessel.

TABLE 2

Determination of Reaction Rate Constant at a Pressure of 500 kg/cm^2

Experiment 5 $a=0,5090;\ b=0,5046$			Experiment 6 $a=0,4999;\ b=0,4679$			Experiment 7 $a=0,5039;\ b=0,4999$		
τ in min	x in mole/liter	$k\cdot10^4$ in liter·mole^{-1}·min^{-1}	τ in min	x in mole/liter	$k\cdot10^4$ in liter·mole^{-1}·min^{-1}	τ in min	x in mole/liter	$k\cdot10^4$ in liter·mole^{-1}·min^{-1}
120	0,0383	13,2	120	0,0331	12,4	120	0,0392	13,8
240	0,0753	14,1	240	0,0644	13,0	240	0,0722	13,7
360	0,1057	14,2	360	0,0966	14,1	360	0,0995	13,4
480	0,1312	14,1	480	0,1138	13,0	480	0,1258	13,7

TABLE 3

Determination of Reaction Rate Constant at a Pressure of 1000 kg/cm^2

Experiment 8 $a=0,4954;\ b=0,5010$			Experiment 9 $a=0,4962;\ b=0,5007$			Experiment 10 $a=0,4938;\ b=0,5007$		
τ in min	x in mole/liter	$k\cdot10^4$ in liter·mole^{-1}·min^{-1}	τ in min	x in mole/liter	$k\cdot10^4$ in liter·mole^{-1}·min^{-1}	τ in min	x in mole/liter	$k\cdot10^4$ in liter·mole^{-1}·min^{-1}
90	0,0334	15,2	120	0,0533	19,0	90	0,0365	16,8
180	0,0694	17,2	210	0,0845	18,5	180	0,0708	17,6
270	0,1006	17,9	300	0,1124	18,5	270	0,1005	17,9
360	0,1296	18,6	392	0,1391	18,8	360	0,1274	18,3
450	0,1494	18,2	480	0,1663	19,9	450	0,1595	20,0

The first two terms of the series were normally used for the calculation; in this case the error in the calculations caused by neglecting the other terms in the series was less than the experimental error. In the calculation of the rate constant, allowance was made for the change in concentration due to compression and the elevation of the temperature to 50° (data on the compressibility of alcohol was taken from [9]). The results of measuring the reaction rate constants are given in Tables 1-4. The values of a, b, and x were determined at atmospheric pressure and 20°.

The slight tendency of the values of the constant calculated according to Eq. (2) (see the last column in Tables 1-4) to increase with an increase in the duration of the experiment is explained by the fact that the

TABLE 4

Determination of Reaction Rate Constant at a Pressure of 2000 kg/cm^2

Experiment 11 $a=0.5006;\ b=0.5012$			Experiment 12 $a=0.5022;\ b=0.4999$			Experiment 13 $a=0.4975;\ b=0.5000$		
τ in min	x in $\frac{\text{mole}}{\text{liter}}$	$k \cdot 10^4$ in liter $\cdot$ mole^{-1} $\cdot$ min^{-1}	τ in min	x in $\frac{\text{mole}}{\text{liter}}$	$k \cdot 10^4$ in liter $\cdot$ mole^{-1} $\cdot$ min^{-1}	τ in min	x in $\frac{\text{mole}}{\text{liter}}$	$k \cdot 10^4$ in liter $\cdot$ mole^{-1} $\cdot$ min^{-1}
61	0,0471	30,7	62	0,0491	31,7	60	0,0441	29,3
120	0,0867	31,5	120	0,0921	33,9	120	0,0838	30,6
						180	0,1184	31,4
183	0,1321	35,3	180	0,1307	35,4	241	0,1487	32,0
						300	0,1746	32,6

solution poured into the reactor acquired the necessary temperature only after a few minutes (as was confirmed by direct measurements of the solution temperature). Therefore, to find the true value of the rate constant we plotted the data obtained on a graph in the coordinates $[1/(a-x) + B, \tau)]$ where $B = [(a-b)/2] \cdot [1/(a-x)^2 - 1/a^2]$. This gave straight lines (Fig. 1) whose slopes were used to calculate the reaction rate constants at different pressures. The first points in each experiment lay slightly above the line for the reason given above.

DISCUSSION OF EXPERIMENTAL RESULTS

The results of determining the rate constants of the reaction we studied at different pressures, obtained by the graphical method described above, are given in Table 5.

An examination of Table 5 shows that the reaction rate constant increased considerably with an increase in pressure.

TABLE 5

Pressure Dependence of Rate Constant (t = 50°)

P in kg/cm^2	$k_1 \cdot 10^4$ in liter $\cdot$ mole^{-1} $\cdot$ min^{-1}
1	18.80
500	13.2
1000	38.7
2000	2.8

The literature [10-12] contains reports that in Menshutkin reactions, together with the main process

$$R_3N + R'Hal \xrightarrow{k_1} R_3NR'Hal \qquad (a)$$
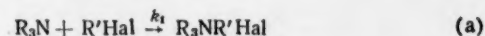
there is the possibility of the autocatalytic reaction

$$R_3N + R'Hal + R_3NR'Hal \xrightarrow{k_2} 2R_3NR'Hal \qquad (b)$$
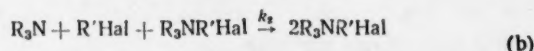
With the reaction in alcohol solution it is also necessary to consider alcoholysis of the alkyl halide:

$$R'Hal + R''OH \xrightarrow{k_3} R'OR'' + HHal \qquad (c)$$
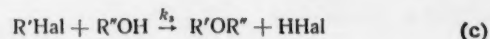
The presence of the autocatalytic reaction (b) would lead to high values for the rate constant calculated from Eq. (2) and the value of this constant would increase as the reaction products accumulated.

On the other hand, the occurrence of alcoholysis (c) should lead to low values for the reaction rate constant calculated from Eq. (2) and this constant should decrease in value with an increase in the duration of the experiment.

We carried out the alcoholysis of C_2H_5I in absolute ethanol at 50° and atmospheric pressure. The initial C_2H_5I concentration in the solution was 0.5 M. After definite time intervals, 10 ml samples of solution were withdrawn and the HI liberated was titrated with Ba(OH)$_2$ solution.

The rate constant k_3 was found to be extremely low and equal to $\sim 1 \cdot 10^{-5}$ min^{-1}. Free iodine was also liberated during the reaction and the amount of this was determined by titration with Na$_2$S$_2$O$_3$ solution. If it is assumed that all the iodine determined by this method was formed from HI liberated as a result of reaction (c), the constant k_3 is increased by a factor of approximately two.
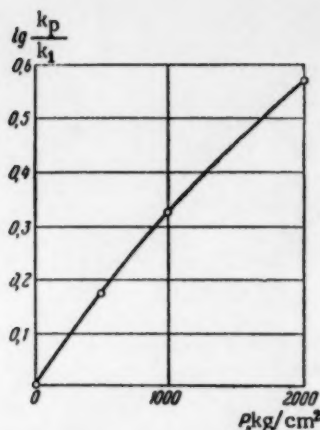
Fig. 2. Pressure dependence of rate constants. k_p and k_1 are the rate constants at the pressure P and atmospheric pressure, respectively.

It may be shown that such a value for the rate constant of C_2H_5I alcoholysis leads to a decrease in the value of the reaction rate constant calculated from Eq. (2) by not more than 2% (at the maximum measured conversion). This deviation is within the limits of our possible measurement error. The literature [13] also contains data on the alcoholysis rate of alkyl halides in alcohol solutions which indicate that the rate constants of these reactions increase by a factor of 2-3 with an increase in pressure from atmospheric to 2000 kg/cm^2. As the data in Table 5 show, the value of k_1 increases by a factor of 3.8 over this pressure range. Thus, the inaccuracy in the determination of k_1 has no appreciable effect on the value of $\Delta v^{\neq}$ calculated from Eq. (1). The fact that on graphs of $[1(a-x)+B, \tau]$ at all the pressures investigated the results we obtained lie on straight lines indicates that reaction (b) does not occur to an appreciable extent under the conditions we studied.

Figure 2 shows the pressure dependence of the logarithm of the rate constant. The slope of this curve may be used to calculate the value of $\Delta v^{\neq}$, i.e., the change in volume on the formation of 1 mole of activated complex, by means of Eq. (1). The values obtained are given below:

Pressure in kg/cm^2	1	500	1000	2000
$-\Delta v^{\neq}$ in cc/mole	27.8	22.6	19.1	14.9

Thus, the value $(-\Delta v^{\neq})$ decreased by a factor of almost two with an increase in pressure from atmospheric to 2000 kg/cm^2.

SUMMARY

1. The kinetics of the reaction of pyridine with ethyl iodide in ethanol at 50° and pressures of 1, 500, 1000, and 2000 kg/cm^2 were studied.

2. The volume changes of the system on the formation of one mole of activated complex in the reaction studied under the given conditions were calculated.

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HOMOGENEOUS CATALYSIS IN THE GAS-PHASE OXIDATION OF HYDROCARBONS

COMMUNICATION 1. NATURE OF THE TWO HEAT-EVOLUTION MAXIMA

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The chain and autocatalytic nature of the gas-phase oxidation of hydrocarbons makes possible the wide use of homogeneous catalysts both for accelerating the process and for changing the direction of the reaction [1, 2]. Nitrogen oxides always play a special role in homogeneous catalysis [3-5].

Émanuél' and Maizus [6], starting from ideas on macroscopic stages, showed that in the oxidation of propane in the presence of nitrogen dioxide, two heat-evolution maxima are observed during the reaction. The appearance of two heat-evolution maxima during the oxidation of methane in the presence of NO_2 was first reported by Polyakov and Urizko [7]. Similar phenomena were observed by Émanuél', Markevich, and Maizus in the oxidation of propane [8] and by Émanuél' and Sedova [9] in the oxidation of ethane in the presence of a homogeneous catalyst.

According to the ideas of Polyakov [10], the first heat-evolution maximum in the oxidation of methane is connected with the formation of formaldehyde as the time at which the first heat-evolution maximum appears and the time of the maximum formaldehyde concentration coincide. The second heat-evolution maximum is connected with the homogeneous oxidation of the heterogeneous decomposition products of formaldehyde, hydrogen and carbon monoxide. From these ideas of Polyakov it follows that the appearance of the two heat-evolution maxima is not connected with the specific action of added NO_2. In this case two heat-evolution maxima should also appear in the oxidation of methane without NO_2 added, which has never been observed.

In the case of propane oxidation in the presence of HBr, Émanuél' and Maizus predicted and explained the phenomenon of two heat-evolution maxima starting from the theory of the initial initiating reaction [11]. According to this theory an initial branched chain reaction forms some intermediate substance I_0, which then decomposes monomolecularly, initiating chains of length $\underline{v}$. Thus, there are two macroscopic stages: the first a branched one and the second unbranched. However, during a complex reaction in two macroscopic stages, two heat-evolution maxima may be observed either in the case when both stages are autocatalytic or in the case when each of them is a complex process occurring in several successive stages.

This may be demonstrated on the example of a simple, nonautocatalytic reaction of the first order. Let us examine a reaction occurring in two stages:

$$A \rightarrow B \quad (1)$$
$$B \rightarrow C \quad (2)$$
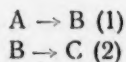
where Q_1 and Q_2 are the heat effects of reactions (1) and (2) and k_1 and k_2 are the rate constants of these reactions. The experimentally measured temperature difference between the center and the wall of the reaction vessel ΔT is proportional to the heat-evolution rate, which, in its turn, is proportional to the reaction rate:

$$\Delta T \sim (Q_1 w_1 + Q_2 w_2), \tag{1}$$

where w_1 and w_2 are the rates of reactions (1) and (2).

The rate of reaction (1):

$$w_1 = k_1 A_0 e^{-k_1 t}, \tag{2}$$

where A_0 is the initial concentration of substance A.

The rate of reaction (2):

$$w_2 = \frac{k_1 k_2 A_0}{k_2 - k_1} (e^{-k_2 t} - e^{-k_1 t}). \tag{3}$$

By substituting w_1 and w_2 in Eq. (1) and differentiating it with respect to time we obtain:

$$\frac{d(\Delta T)}{dt} \sim \frac{k_2^2}{k_2 - k_1} Q_2 e^{-k_2 t} - \left(k_1 Q_1 + \frac{k_1 k_2 Q_2}{k_2 - k_1} \right) e^{-k_1 t} . \tag{4}$$

Equation (4) shows that with the reaction occurring in two stages (both stages nonautocatalytic), independent of the relation between k_1 and k_2 and Q_1 and Q_2, the heat-evolution rate can only have one maximum. The time at which the heat-evolution maximum appears will be given by the equation:

$$t_{max} = \frac{1}{k_2 - k_1} \ln \frac{k_2^2 Q_2}{k_1 (k_2 - k_1) Q_1 + k_1 k_2 Q_2}.$$

Calculations show that if the first stage is autocatalytic and the second is not, there will be only one maximum. If the first stage is nonautocatalytic and the second autocatalytic, the curve of the heat-evolution rate may have one minimum and one maximum.

Thus, although the idea of Émanuél' on macroscopic stages satisfactorily explains the appearance of two heat-evolution maxima in principle, it is still necessary to determine which of these macroscopic stages is autocatalytic, which of the chemical processes occur in the first and second stages, etc. To solve all these problems it is most convenient to investigate the oxidation of the simplest hydrocarbon, namely, methane.

EXPERIMENTAL

The experiments were carried out in a normal vacuum kinetic apparatus with a specially designed reactor, fitted for differential calorimetry by Koval'skii's method [12]. The temperature difference between the center and the wall of the reaction vessel was measured with the aid of a highly sensitive galvanometer.

Figure 1 shows characteristic kinetic curves of the change in pressure and heat-evolution rate during the oxidation of methane in a stoichiometric mixture with oxygen at 465°, a pressure of 225 mm, and an NO_2 concentration of 1%. The reaction practically begins without an induction period and is complete (according to ΔP) at the moment at which the second maximum appears. The height, width, and relative position of the first and second maximum may change, depending on the experimental conditions (temperature, pressure, catalyst concentration, etc.).

Figure 2 gives kinetic curves of the change in pressure and ΔT in relation to the total pressure of the starting stoichiometric mixture (containing 1% of NO_2) at 465°. With an increase in the total pressure, the magnitude of the first maximum increases, but the time at which it appears does not change. With an increase in pressure the second maximum is displaced toward longer contact times and the absolute peak size increases simultaneously.

Fig. 1. Time dependence of ΔP and ΔT for the mixture $CH_4 + 2O_2 + 1\%$ NO_2 at $T = 465°$ and $P = 255$ mm.

Fig. 2. Dependence of ΔP and ΔT on the total mixture pressure in the reaction, vessel for the mixture $CH_4 + 2O_2 + 1\%$ NO_2 at $T = 465°$: 1) 100 mm; 2) 150 mm; 3) 205 mm; 4) 270 mm.

With a change in the concentration of the homogeneous catalyst NO_2 with a constant pressure of starting mixture, the opposite picture is observed: with an increase in the NO_2 concentration, the time at which the second maximum appeared decreases (Fig. 3). The fact that the time at which the first maximum is reached is independent of NO_2 concentration (Figs. 2 and 3) indicates that the maximum observed experimentally is apparently connected with the inertia of the galvanometer. Since the measurement of ΔT begins with zero, the first maximum will always appear experimentally, regardless of the true form of the kinetic curve, as is shown by Fig. 4a. If the relaxation time of the galvanometer is large, then the observed maximum will always be less than the true one (Fig. 4b).

A kinetic study of the gas-phase nitration of hydrocarbons shows that the reaction of NO_2 with methane under our experimental conditions occurs after a few seconds. The oxidation of methane without NO_2 under the same conditions proceeds extremely slowly. We showed that at $T = 465°$ and a reaction mixture pressure of 225 mm, the induction period reaches 20 min. In the presence of NO_2, the reaction is complete after a few minutes.

Starting from a combination of these experimental facts, we derived a working hypothesis which satisfactorily explains the nature of the two heat-evolution maxima in the catalytic oxidation of hydrocarbons; its main features coincide with the theory of the initial initiating reaction of Émanuél' [11]. According to this hypothesis the first heat-evolution maximum is connected with the rapid (at these temperatures) reaction of NO_2 with methane. The second maximum is the result of the oxidation of methane, which is strongly catalyzed by some products formed during the reaction of methane with nitrogen oxides. The present work is devoted to checking the accuracy of this hypothesis.

If our hypothesis is true, then during the reaction of methane with NO_2 (without oxygen) under our conditions, only the first maximum should appear and this was actually observed experimentally (Fig. 5, curve 1). For pure methane (Fig. 5, curve 2) and a mixture of methane and NO (Fig. 5, curve 3) maxima were also obtained, but their size was considerably less and they could have been produced by the sensitivity of the galvanometer. A comparison of ΔT for the given mixtures indicates that in the case of the mixture of methane and NO_2, actual heat evolution was recorded.

The addition of a certain amount of oxygen to the mixture $CH_4 + NO_2$ should produce an oxidation reaction, which, in its turn, should lead to the appearance of a second maximum on the heat-evolution curve. Figure 6 shows that with an increase in the oxygen concentration, the oxidation reaction is intensified and finally a second maximum appears even though the NO_2 concentration falls slightly. Attention is attracted by the fact that despite the fall in the NO_2 concentration, the first maximum increases with an increase in the oxygen content. This may be explained by two factors: 1) with an increase in oxygen concentration the equilibrium in the reaction $2NO + O_2 \rightleftharpoons 2NO_2$ is displaced to the right and the NO_2 concentration increases; 2) in the region of the first maximum, together with the reaction of NO_2 with methane, the oxidation reaction may occur simultaneously.

If the first peak is actually caused by the reaction of CH_4 with NO_2 and the second by the oxidation of methane, then apparently there must be some other substances (catalysts) which, under our conditions (temperature

Fig. 3. Dependence of ΔP and ΔT on the NO_2 concentration in the reaction mixture of $CH_4 + 2O_2$ at $T = 465°$ and $P = 225$ mm: 1) NO_2 1%; 2) NO_2 0.9%; 3) NO_2 0.82%; 4) NO_2 0.73% 5) NO_2 0.66%.
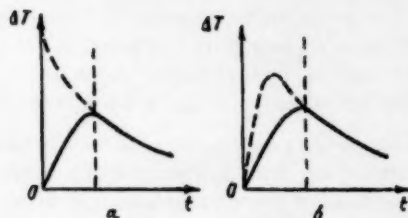
Fig. 4. Position of observed heat-evolution maximum in relation to the form of the kinetic curve: a) true curve has no maximum; b) true curve has maximum.

and pressure), react with methane at a greater rate than the oxidation of methane catalyzed by them. In this case two heat-evolution maxima should appear. Such catalysts were found to be Cl_2, Br_2, HCl, and HBr. The changes in ΔT with time in the reactions of Cl_2 and Br_2 with methane are shown in Figs. 7 and 8. Figure 9 clearly shows the appearance of a second maximum during the oxidation of methane catalyzed by Br_2.

If our hypotheses are correct, there should be processes in which NO_2 does not react (or reacts slowly) with the substance undergoing oxidation. Such a process was found to be the homogeneous oxidation of methyl alcohol. The nitration of alcohols is known to be a slow process. Therefore, the addition of large amounts of NO_2 to a mixture of methyl alcohol and oxygen has a weak effect on the oxidation, but leads to the appearance of a second maximum, connected with the reaction of NO_2 with secondary oxidation products, the reactions of which are apparently strongly catalyzed by NO_2. Figure 10 clearly shows the appearance of a second maximum after the maximum characterizing the oxidation of methyl alcohol itself.[*]

In the work of Polyakov [7], it was shown that treatment of the reaction vessel walls with potassium tetraborate eliminates the second maximum. This sharply contradicts our ideas according to which the second maximum is connected with the oxidation of methane. In repeating Polyakov's experiments, we demonstrated that quite a small increase in temperature is sufficient for the second maximum to reappear (Fig. 11). Consequently, potassium tetraborate affects only the subsequent oxidation reaction.

Thus, the appearance of two heat-evolution maxima in the oxidation of methane with NO_2 added is connected with the reaction of NO_2 with methane (first maximum) and the subsequent oxidation of methane to the final products (second maximum). Evidently the reaction of NO_2 with methane forms some sort of intermediate substance which then catalyzes the oxidation of methane. Careful chemical analysis of the reaction products from methane showed that this substance is nitromethane. Polarographic analysis showed that approximately one half of the NO_2 introduced is converted to nitromethane.

If it is correct to state that the first reaction is connected with the formation of nitromethane and the second with the oxidation, which is catalyzed by nitromethane, then addition of nitromethane to a methane-

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[*] Data on the oxidation of methyl alcohol were taken from the diploma work of the student I. Bel'govskii.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.

Fig. 5. Relation between ΔT and contact time for the mixtures $CH_4 + NO$ and $CH_4 + NO_2$ at $T = 465°$ and $P = 225$ mm: 1) $CH_4 + 20\%$ NO_2; 2) pure CH_4; 3) $CH_4 + 20\%$ NO.

Fig. 6. Time dependence of ΔT for the mixture $CH_4 + NO_2$ with oxygen added at $T = 465°$ and $P = 225$ mm; 1) pure methane; 2) $CH_4 + 4\%$ NO_2; 3) $CH_4 + 3.6\%$ $NO_2 + 10\%$ O_2; 4) $CH_4 + 3.25\%$ $NO_2 + 20\%$ O_2; 5) $CH_4 + 2.92\%$ $NO_2 + 30\%$ O_2; 6) $CH_4 + 2.64\%$ $NO_2 + 40\%$ O_2; 7) $CH_4 + 2.37\%$ $NO_2 + 50\%$ O_2.

Fig. 7. Time dependence of ΔT with addition of chlorine to methane at $T = 465°$ and $P = 225$ mm: 1) pure methane; 2) $CH_4 + 6$ mm Cl_2; 3) $CH_4 + 10$ mm Cl_2; 4) $CH_4 + 25$ mm Cl_2.

Fig. 8. Time dependence of ΔT for the mixture $CH_4 + Br_2$ at $T = 465°$ and $P = 225$ mm: 1) 9.2% Br_2; 2) 4.6% Br_2; 3) 2.3% Br_2; 4) pure CH_4.
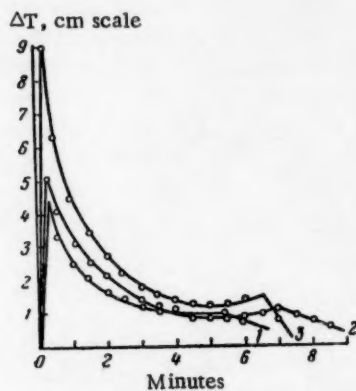
Fig. 9.
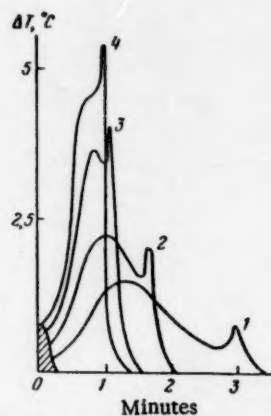
Fig. 10.

Fig. 9. Time dependence of ΔT for the reaction of $CH_4 + 2O_2$ at $T = 465°$ and $P = 225$ mm with Br_2 added: 1) traces of bromine; 2) 4% Br_2; 3) 10% Br_2.

Fig. 10. Effect of nitrogen oxides on the oxidation of methyl alcohol in a quartz vessel at $T = 480°$ and $P = 105$ mm; mixture: $CH_3 OH -$ 52.5 mm and $O_2 - 52.5$ mm: 1) 0.3% NO_2; 2) 0.52% NO_2; 3) 0.67% NO_2; 4) 0.79% NO_2.

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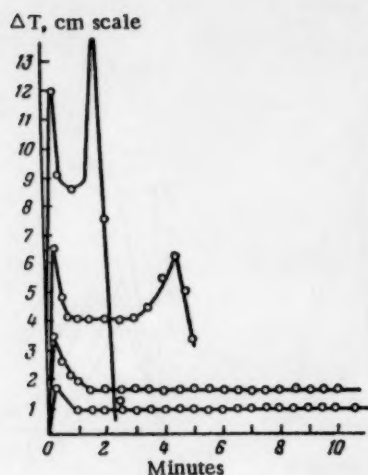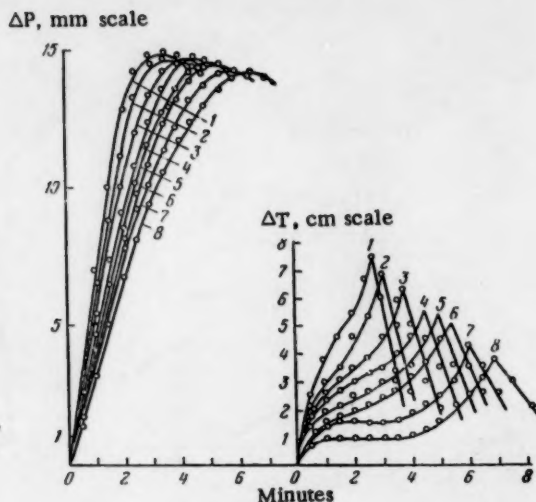
Fig. 11.

Fig. 12.

Fig. 11. Time dependence of ΔT for the reaction of $CH_4 + 2O_2 + 1\%$ NO_2 with the surface of the vessel treated with potassium tetraborate; $P = 225$ mm; the lower curve corresponds to $T_1 = 442°$; the second to $T_2 = 465°$; the third to $T_3 = 491°$; the fourth to $T_4 = 515°$.

Fig. 12. Dependence of ΔP and ΔT on the nitromethane added to the reaction mixture at $T = 465°$ and $P = 225$ mm in the following amounts: 1) 3%; 2) 27%; 3) 245%; 4) 2.21%; 5) 1.99%; 6) 1.8%; 7) 1.62%; 8) 1.46%.
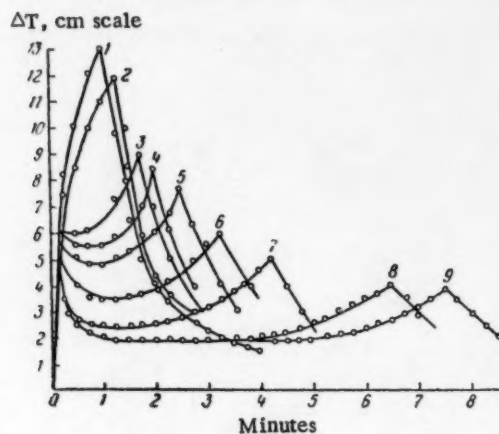
Fig. 13. Time dependence of ΔT for the mixture $CH_4 + 2O_2 + 1\%$ NO_2 at $T = 465°$ and $P = 225$ mm with the addition of various amounts of nitromethane: 1) 8 mm; 2) 7.2 mm; 3) 6.5 mm; 4) 5.85 mm; 5) 5.25 mm; 6) 4.73 mm; 7) 4.25 mm; 8) 3.81 mm; 9) 0 mm.

oxygen mixture should cause the appearance of only the second maximum. Figure 12 gives kinetic curves of heat evolution in relation to nitromethane concentration. With an increase in the nitromethane concentration, the time of appearance of the second maximum shortens and the size of this maximum increases.

If NO_2 is added to the mixture $CH_4 + 2O_2 + CH_3NO_2$, the first heat-evolution maximum should appear as independent of the oxidation reaction, NO_2 reacts with methane, leading to the formation of the first maximum.

Figure 13 shows heat-evolution curves for the mixture $CH_4 + 2O_2 + 1\%$ NO_2 with various amounts of CH_3NO_2 added. With a decrease in the nitromethane concentration the first maximum is formed and then the oxidation reaction proceeds, leading to the appearance of the second maximum.

A detailed investigation of the effect of CH_3NO_2 on methane oxidation will be the subject of next communication.

SUMMARY

1. The kinetics of heat evolution during the oxidation of methane in the presence of NO_2 and CH_3NO_2 were investigated.

2. It was established that the presence of two heat-evolution maxima is connected with the reaction of NO_2 with methane (first maximum) and the oxidation of methane (second maximum).

3. The homogeneous catalysts Cl_2, Br_2, HCl, and HBr also give two heat-evolution maxima.

4. The reaction of NO_2 with methane forms nitromethane, which catalyzes the oxidation of methane.

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* Original Russian pagination. See C. B. Translation.

PHYSICAL AND CHEMICAL PROPERTIES OF WS$_2$ CATALYSTS

COMMUNICATION 5. CATALYTIC ACTIVITY OF AN UNMIXED WS$_2$ CATALYST
FOR THE HYDROGENATION OF PHENOL

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In previous communications [1, 2] the results were given of a detailed determination of the chemical and phase compositions and porous and crystal structures of unmixed WS$_2$ catalysts. Naturally, an attempt was made to find a connection between these properties and, in the first instance, the sulfur content, i.e., the atomic ratio S : W, and the catalytic activity and also to determine the specific activity of an unmixed WS$_2$ catalyst, as no such data are available in the literature. In addition, it seemed interesting to compare the activity with the acidity of a WS$_2$ catalyst.

EXPERIMENTAL

In addition to the previously described [1, 2] samples of unmixed WS$_2$ catalyst (1, 3, 3_{400}, 4, 5, 6_{400}, 7, 7_{400}, 8, 8_{400}, 9_{20} and 14), in the present work we also investigated samples 10 and 12, which were prepared by decomposition of different portions of $(NH_4)_2WS_4$ and used in industrial destructive hydrogenation. During the investigation, the WS$_2$ catalysts were pumped out in high vacuum at 400°. Heating was begun only after a residual pressure of no higher than $5 \cdot 10^{-5}$ mm Hg had been reached and the temperature was raised at ~200°/hr. The samples were kept at 400° and $5 \cdot 10^{-5}$ mm for not less than 10 hr and then cooled at a rate of ~150°/hr. The pumped-out WS$_2$ catalysts were denoted by the previous number but with the addition of an index indicating the temperature of the thermal treatment in vacuum. Sample 13_{400} was obtained from sample 12, which, before pumping out (at 400°) was placed in a large excess of benzene for a week. Sample 9_{20} was obtained from sample 3 by treatment with carbon disulfide and pumping out at 20°, as was described in detail in [2].

Data on the composition, specific surface, and acidity of the samples investigated are given in Table 1. The atomic ratio S : W was calculated from elementary-analysis results obtained in the Analytical Laboratory of the Institute of Organic Chemistry, for which we are very grateful. With the exception of sample 9_{20}, the specific surface of WS$_2$ catalysts was determined from the adsorption of nitrogen vapor at the boiling point of liquid nitrogen and calculated by the Brunauer, Emmett, and Teller method, as was described in detail for samples 3_{400}, 6_{400}, 7_{400} and 8_{400} in our previous work [1]. The corresponding value for sample 9_{20} was obtained by means of the dynamic method of Rubinshtein and Afanas'ev [3, 4] by the adsorption of benzene at 20° ($\omega_0 = 40$ A^2).*

For the determination of acidity, samples of WS$_2$ catalyst were kept for several days in ten times their weight of distilled water and the H⁺ ion content determined by titration of the aqueous extract with 0.1 N NaOH

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* These two methods gave similar values for the specific surface of WS$_2$ catalysts that did not contain excess sulfur; for example, S determined by the dynamic method for sample 1_{400} equaled 58 m^2/g.

TABLE 1

Composition, Specific Surface, and Acidity of Unmixed WS_2 Catalysts Investigated

Catalyst No.	Atomic ratio S:W	Specific surface, in m^2/g	Acidity in equivalents of H·/mole
1	2,27		$0,79 \cdot 10^{-3}$
1_{400}		65	$0,1 \cdot 10^{-3}$
3	2,30	3	$1,46 \cdot 10^{-3}$
3_{400}	2,006	66	$0,29 \cdot 10^{-3}$
4	1,92		$1,24 \cdot 10^{-3}$
4_{400}	1,53	49	0,0
5	2,25		$0,81 \cdot 10^{-3}$
5_{400}		50	
6	2,16		$0,35 \cdot 10^{-3}$
6_{400}	2,03	54	
7	2,08		$0,21 \cdot 10^{-3}$
7_{400}	1,97	23	
8	2,05		$0,14 \cdot 10^{-3}$
8_{400}	1,97	3	
9_{20}	1,96	64	
10	2,14		$1,56 \cdot 10^{-3}$
10_{400}		46	
12	2,08		$0,42 \cdot 10^{-3}$
12_{400}		31	
13_{400}	2,00	40	

solution with Methyl orange. A second aqueous extract was neutral to this indicator. On the example of samples 3 and 4 it was shown that samples of the same catalyst which had been ground differently and stored under different conditions had exactly the same acidity. Consequently, the measured acidity was not conditional, but was a characteristic property of each sample investigated.

For comparing the catalytic activity we chose the high-pressure hydrogenation of phenol under conditions close to the operating conditions of a WS_2 catalyst in industry, namely, at 380° and a partial pressure of H_2 of ~220 atm. The reaction was carried out in a 0.5 liter rotating autoclave into which was placed "pure" grade crystalline phenol and the catalyst sample investigated. In all experiments the starting amount of phenol was 30 g and of catalyst, 1 g, and the initial hydrogen pressure was 110 ± 6 atm. The reaction conditions were strictly identical: heating to 380 ± 10° over 1 hr, the autoclave kept at this temperature for 1 hr, and then cooling with continuous rotation. The H_2 pressure in the autoclave was measured with an accuracy of ± 1 atm and the temperature, ± 3°. To the liquid reaction products was added 100 ml of 15% NaOH solution and the aqueous alkaline extract filtered and used for determination of the amount of unreacted phenol by titration with bromide-bromate solution [5, 6].

The reproducibility of the results was very good; it was checked on catalysts 3, 4, 10, 12, and 14 (Table 2). The activity of the catalysts investigated could be determined from the H_2 consumption with an error which did not exceed ± 1 atm.

Table 3 gives experiments with samples 3 and 4, which were powdered and separated into different fractions by sieving, and these show that beginning with grain dimensions of 1-2 mm, the diffusion of molecules * in the catalyst pores hardly affects its operation and with further grinding of the catalyst, the reaction passes completely into the kinetic region. We therefore used finely powdered catalysts, and only in certain cases was their grain size 1-2 mm.

The results of determining the activity of the WS_2 catalyst samples investigated are given in Table 4. The relation of the amounts of phenol and hydrogen reacted to the specific surface of pumped-out WS_2 catalysts is shown in Fig. 1.

In a study of the effect of the composition of WS_2 catalysts on their activity, experiments were carried out in which to 1 g of catalyst (samples 3, 3_{400}, 4, and 4_{400}) was added a very small amount of carefully ground stick sulfur (0.043-0.046 g when the atomic ratio S:W in the mixture 3_{400} + S was close to that in catalyst 3). In a parallel experiment (under standard conditions) in the presence of sulfur alone (0.103 g), 0.7 g of phenol reacted and the H_2 absorption was 4 atm.

DISCUSSION OF EXPERIMENTAL RESULTS

The effect of phase composition, determined by x-ray diffraction, on activity was discussed in our previous article [2]. Meanwhile, until the present work the relation of the activity and selectivity of a WS_2 catalyst to its sulfur content had not been investigated at all. Therefore, the closely connected problem of the reason for the increase in the catalyst activity in destructive hydrogenation as a result of the addition of sulfur to the raw material remained completely unsolved. We were the first to investigate these problems, which are very

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* Phenol was in the vapor state in all experiments, as at 382° its saturated vapor pressure is 40 atm (t_{cr} = 419°) [7].

TABLE 2

Check on Reproducibility of Results in the Determination of the Activity of WS_2 Catalysts in Phenol Hydrogenation under Pressure (grain size 2.0-1.0 mm)

Catalyst No.	Amount of phenol P in g		H_2 pressure in atm			$\Delta H_2/\Delta P$ in moles of H_2 per mole of P
	unreacted	reacted	initial	after experiment	consumption during reaction	
3	5,5	24,5	108	83	25	2,0
3	4,7	25,3	106	80	26	2,0
4	7,7	22,3	108	89	19	1,7
4	9,2	20,8	112	94	18	1,7
10 ⎫	4,4	25,6	109	86	23	1,8
10 ⎬ Dust	5,4	24,6	109	86	23	1,8
12 ⎭	12,0	18,0	105	89	16	1,8
12	12,7	17,3	112	96	16	1,8
14	19,1	10,9	110	102	8	1,4
14	18,9	11,1	109	100	9	1,6

TABLE 3

Activity of WS_2 Catalysts in Phenol Hydrogenation under Pressure at Various Degrees of Grinding

Catalyst No.	Grain size in mm	Amount of phenol P in g		H_2 pressure in atm			$\Delta H_2/\Delta P$ in moles of H_2 per mole of P
		unreacted	reacted	initial	after experiment	consumption during reaction	
3	5—3	12,6	17,4	109	87	22	2,5
3	2—1	5,1	24,9	107	81	26	2,1
3	0,5 —0,25	4,1	25,9	109	80	29	2,2
3	0,15—0,08	3,5	26,5	110	82	28	2,1
3	Dust	2,9	27,1	110	81	29	2,1
4	5—3	17,1	12,9	111	100	11	1,7
4	2—1	8,5	21,5	111	92	19	1,7
4	Dust	9,0	21,0	110	91	19	1,8

interesting from the theoretical and practical points of view, and though much remains to be solved, a series of fundamental conclusions can be drawn from the data obtained.

Thus, our experiments showed that under otherwise equal conditions a WS_2 catalyst with $S:W > 2$ is more active than a catalyst with $S:W < 2$, i.e., than a catalyst with excess, nonstoichiometric tungsten (cf., for example, samples 4 and 5 which have identical specific surface* and similar acidity). We established that the activity of a WS_2 catalyst is increased only by sulfur atoms lying on its surface; sulfur in the pores of the catalyst has no effect on its activity. In actual fact, as Table 4 shows, the activity of sample 3 with $S:W = 2.30$ was completely unchanged after all the excess sulfur had been extracted from it with carbon disulfide (sample 9_{20}). The role of surface sulfur atoms is also indicated by the fact (which we established for the first time) that the activity of a mixture of WS_2 catalyst + S in hydrogenation is appreciably greater than the sum of the activities of its components separately. Moreover, from the literature it is known that when sulfur is added to the raw material, the activity of the catalyst is increased only up to a definite limit [8], which we consider is reached when the surface is completely sulfurized. For this reason, the promoting action of added elementary sulfur in our experiments decreased with an increase in the excess, nonstoichiometric sulfur content of the WS_2 catalyst (cf., for example, the activity of the mixture 3_{400} + S and 3 + S). It may be considered that in comparison with catalysts with $S:W > 2$, catalysts with $S:W < 2$ have a lower content of sulfur atoms on the surface and this causes their lower activity.

*After pumping out at 400°.

TABLE 4

Activity of Unmixed WS_2 Catalyst Investigated in Hydrogenation under Pressure (in 0.5 liter autoclave) 30 g of phenol at 380°, 1 g of catalyst*

Catalyst No.	Grain size in mm	Amount of phenol P in g		H_2 pressure in atm			$\Delta H_2/\Delta P$ in moles of H_2 per mole of P
		unreacted	reacted	initial	after experiment	consumption during reaction	
1	2—1	4,7	25,3	108	83	25	1,9
1_{400}	Dust	6,2	23,8	113	95	18	1,5
3	"	2,9	27,1	110	81	29	2,1
3_{400}	"	7,3	22,7	104	84	20	1,7
4	"	9,0	21,0	110	91	19	1,8
4_{400}	"	13,0	17,0	112	99	13	1,5
5	2—1	5,0	25,0	109	88	21	1,7
5_{400}	Dust	7,5	22,5	113	96	17	1,5
6	"	7,3	22,7	114	94	20	1,7
7	"	15,6	14,4	113	106	7	1,0
7_{400}	"	19,2	10,8	114	107	7	1,3
8_{400}	"	25,9	4,1	115	114	1	0,5
9_{20}	"	1,6	28,4	117	88	29	2,0
10	"	4,9	25,1	109	86	23	1,8
10_{400}	"	8,9	21,1	112	97	15	1,4
12	2—1	12,4	17,6	109	93	16	1,8
12_{400}	Dust	14,6	15,4	113	102	11	1,4
13_{400}	"	12,9	17,1	115	103	12	1,4
14	2—1	19,0	11,0	110	101	9	1,6
3+0,046 g S	Dust	0,2	29,8	115	80	35	2,3
3_{400}+0,045 g S	"	1,3	28,7	113	82	31	2,1
4+0,043 g S	"	1,7	28,3	110	82	28	2,0
4_{400}+0,043 g S	"	12,3	17,7	113	89	24	2,7

* Average values for parallel experiments are given.
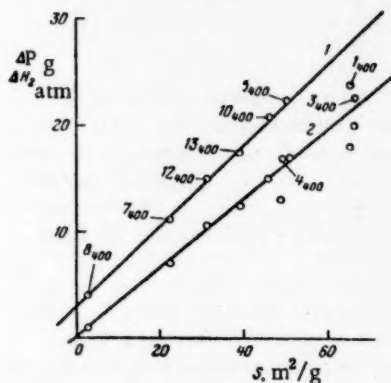
Fig. 1. Relation between the activity of WS_2 catalysts pumped out at 400° and their specific surface (S): 1) amount of phenol reacted (ΔP); 2) amount of hydrogen absorbed (ΔH_2).

The acidity of a WS_2 catalyst, like its sulfur content, appreciably affects its activity.* In actual fact, the activity of a catalyst increases with an increase in acidity. For example, this can be seen particularly clearly by comparing samples 1 and 3, whose specific surfaces and sulfur contents (S : W ratio) are approximately the same.

In considering the change in activity of WS_2 catalyst under the action of thermal treatment at 400° in vacuum, it should be noted that as Table 1 shows, all the excess nonstoichiometric sulfur is removed from catalysts with S : W > 2 under these conditions and as a result of this the S : W ratio becomes close to stoichiometric. In addition, the acidity of the catalysts is decreased appreciably. At the same time, neither recrystallization nor a decrease in specific surface occurs [1, 2].

Table 4 shows that the activity of all the samples investigated decreased as a result of heating in high vacuum at 400°. The decrease in activity was mainly connected with the removal of sulfur from the catalyst, as the mixture 3_{400} + S with an S : W ratio corresponding to the original sample 3 had almost the same activity as the latter. Since, as was shown above, the activity of a catalyst decreases with the removal of only the surface sulfur atoms, the thermal treatment in vacuum evidently removes sulfur from its surface to a greater or lesser extent. The surface of pumped-out catalyst was again

* Since the acidity of a WS_2 catalyst is not determined by its total sulfur content (see Table 1, catalysts 1 and 3, for example), each of these properties affects its activity independently.

The mechanism of the adsorption of unsaturated organic molecules on a WS_2 catalyst during hydrogenation is less clear. Since the adsorption of such a molecule apparently occurs simultaneously on at least two atoms of the catalyst [10, 11], different cases are possible here: adsorption of the organic molecule on only tungsten atoms or on only sulfur atoms, or simultaneously on either of the atoms. It should be noted that in analogy with the hypothesis put forward for hydrogen, in investigating the hydrogenation mechanism it is necessary to consider the possibility of each of these three cases of the adsorption of organic molecules on a WS_2 catalyst. Meanwhile, in [12] Griffith expressed the opinion that in destructive hydrogenation, organic molecules are fixed only on molybdenum atoms in their adsorption on molybdenum sulfide MoS_2. In view of the similarity of the structures and properties of tungsten and molybdenum sulfides, the data we obtained on the relation between the sulfur content and the activity of a WS_2 catalyst showed that this point of view of Griffith is quite inadequately grounded and is only a theoretical or imaginary scheme suitable for the comparison of the activities of MoS_2 and MoO_2 made in his work. It should be added the Griffith compared the total and not the specific activities and this in itself introduces an element of uncertainty due to the lack of allowance for the surface areas of the catalysts compared.

In conclusion it should be noted that, as has already been shown in detail above, the specific activity of a WS_2 catalyst that has not undergone thermal treatment is considerably affected by the acidity, which, at the same time, is not determined by the surface area (see Table 1). Therefore the activity of the original samples of WS_2 catalyst investigated depended on their specific surface not linearly, but in a somewhat more complicated way (Tables 1 and 4).

SUMMARY

1. A comparison was made for the first time of the activity of a series of unmixed WS_2 catalysts, determined from the high-pressure hydrogenation of phenol in the kinetic region at 380° and an initial H_2 pressure of 110 atm, and their chemical composition, crystal structure of the WS_2 phase, specific surface, and acidity.

2. The activity of the WS_2 catalyst in hydrogenation increased with an increase in the sulfur content within the limits of S : W of 1.53 to 2.30 or an increase in acidity.

3. The activity was increased only by sulfur atoms on the surface, while sulfur in the pores did not affect the activity.

4. The specific activity of a WS_2 catalyst with S : W ≈ 2 and an insignificant acidity was independent of the degree of order of the crystalline structure of the WS_2 phase.

5. The composition of the surface affected the selectivity of a WS_2 catalyst; its hydrogenating capacity increased with an increase in the sulfur content.

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TABLE 1

Sample No.	Ni in weight%	400° $\chi_{20°}\cdot10^6$	400° $\chi_{30°}\cdot10^6$	400° $\chi_{160°}\cdot10^6$	600° $\chi_{20°}\cdot10^6$	600° $\chi_{80°}\cdot10^6$	600° $\chi_{160°}\cdot10^6$	750° $\chi_{20°}\cdot10^6$	750° $\chi_{80°}\cdot10^6$	750° $\chi_{160°}\cdot10^6$
					NiO—MgO					
1	2,34	1,08 (50,5)	0,82 (45,4)	0,70 (40,1)	1,12 (58,3)	0,90** (48,8)	0,70**** (40,2)	1,35 (68,0)	1,16 (59,5)	0,87 (47,5)
2	4,60	2,2 (53,1)	1,8 (44,5)	1,6 (40,0)	2,4 (57,5)	2,0 (48,7)	1,65 (41,1)	2,8 (66,2)	2,4 (57,5)	1,9 (46,5)
3	6,00	3,0 (54,0)	2,5 (45,5)	2,2 (40,5)	3,4 (60,5)	2,5** (45,5)	2,1 (38,8)	3,8 (67,2)	3,0** (54,0)	2,6 (47,1)
4	10,40	5,2 (52,0)	4,4 (44,6)	3,7 (37,6)	5,6 (56,0)	4,4** (44,5)	3,7 (37,7)	6,8 (67,5)	5,4 (54,0)	4,8 (48,3)
5	18,65	8,2 (45,0)	7,0 (38,6)	6,0 (33,2)	8,3 (45,6)	7,2 (39,7)	6,2 (33,8)	9,8 (53,5)	8,5 (46,5)	7,3 (40,2)
6	24,20	9,7* (40,8)	8,6 (36,2)	7,5 (31,6)	10,5 (44,0)	9,0 (37,8)	7,7**** (32,6)	12,1 (50,7)	10,5 (44,0)	9,2***** (38,8)
7	20,60	11,3 (38,8)	10,0 (34,4)	9,0 (31,0)	12,0 (41,0)	10,7*** (36,6)	9,5 (32,6)	13,6 (46,5)	12,1** (41,5)	10,8 (37,1)
8	36,00	11,9 (33,4)	10,7 (30,0)	9,8 (27,7)	13,4 (37,6)	12,3 (34,6)	11,0 (30,8)	14,9 (41,8)	13,5** (37,8)	11,9 (33,5)
					NiO—CdO					
9	2,9	1,77 (67,6)	0,86 (38)	0,44 (23,1)	0,30 (18,6)	0,25 (16,9)	0,20 (15,0)	—	—	—
		$\chi_{18°}\cdot10^6$	$\chi_{55°}\cdot10^6$	$\chi_{80°}\cdot10^6$	NiO—ZnO $\chi_{18°}\cdot10^6$	$\chi_{80°}\cdot10^6$	$\chi_{160°}\cdot10^6$	$\chi_{18°}\cdot10^6$	$\chi_{80°}\cdot10^6$	$\chi_{160°}\cdot10^6$
10	3,0	0,57 (32,8)	0,25 (22,2)	0,18 (19,8)	0,25 (22,2)	0,10 (17,2)	0 (13,8)	0,28 (23,2)	0,20 (20,5)	0,11 (17,5)

* 25°.
** 84°.
*** 88°.
**** 165°.
***** 153°. The value of χ per gram of Ni is given in brackets.

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TABLE 2

Firing temperature in °C	$\chi_{Ni} \cdot 10^6$	Δ	μ_B	Firing temperature in °C	$\chi_{Ni} \cdot 10^6$	Δ	μ_B
NiO–CdO				NiO–ZnO			
400	67,6	+200	1,6	400	33,8	+200	1,2
620	17,1	−250	2,1	600	22,7	+ 90	1,5
				750	23,8	−135	2,2
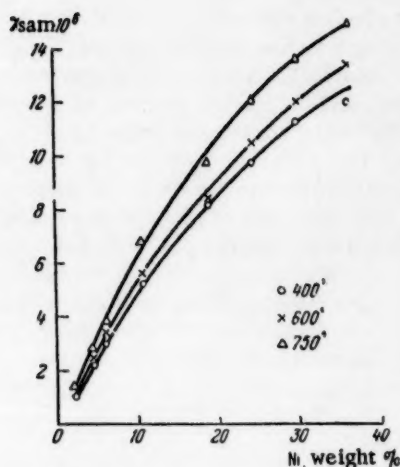
Fig. 1.
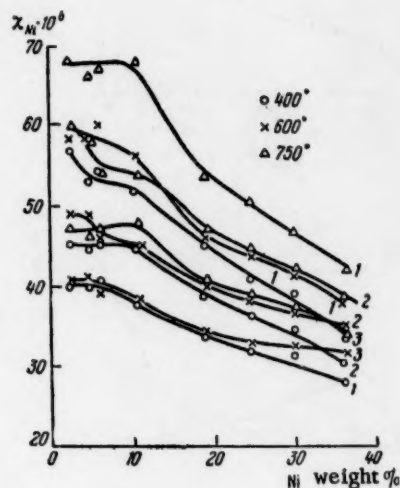
Fig. 2.

160°. The susceptibility of all the samples was independent of field strength over the range of strengths studied. X-ray diffraction patterns of the NiO-MgO catalysts were obtained in RKD cameras on a URS-55 apparatus; the catalysts with a high Ni content were also examined in KMSP camera-monchromators with a curved quartz crystal. The surface was measured by a dynamic method [7] and calculated by the Brunauer, Emmett, and Teller equation.

The catalytic activity of the NiO-MgO catalysts was studied in a flow system on the decomposition of absolute i-C_3H_7OH over the temperature range 320-360°. The i-C_3H_7OH was introduced by means of a transducer-electrolyzer [8] at a space velocity of 2 hr^{-1}. The degree of conversion in most experiments was < 35% and only on the catalyst with 36 weight % of Ni at the highest experimental temperature (360°) did it reach ~63%. Thus, the experiments were carried out far from equilibrium, which is important in studying the kinetics of the process. The completely trappable gaseous products, the volumes of which were reduced to n.p.t., were analyzed on a VTI-1 apparatus. The data on the i-C_3H_7OH decomposition kinetics were processed according to the equation for a reaction in a stream proposed by Balandin and Bork [9].

The results of measurements of the magnetic susceptibility are given in Table 1 and Figs. 1 and 2. Figure 1 shows that the susceptibility per g of sample increased with an increase in the Ni concentration without reaching saturation. Figure 2 shows that the susceptibility per g of Ni changed very little in the initial region of Ni concentrations (up to 10 weight %) and then fell strongly with a further change in concentration. All the catalysts studied obeyed the Curie-Weiss law over the range 20-160°, which made it possible to calculate the change in Δ and μ_B (magnetic moment) with a change in NiO concentration and firing temperature of the catalysts. The results obtained are given in Fig. 3. As this figure shows, in all the series Δ increased with an increase in Ni concentration and the value of Δ in the 400° series was higher than in the 600 and 750° series, which was connected with the higher order of the solid solution at high temperatures and hence the lower value of the
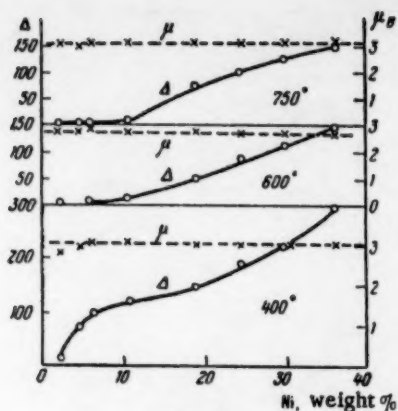
Fig. 3.
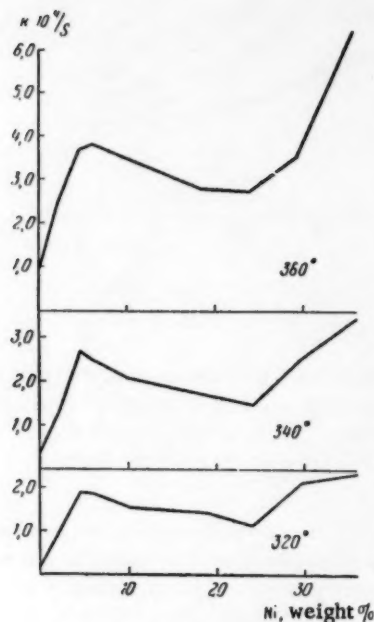
Fig. 4.

paramagnetic environment $\underline{z}$. In all three series of preparations, the magnetic moment was independent of Ni concentration and corresponded to the ion Ni^{2+}.

Table 2 gives the values of Δ and $\cdot\mu_B$, calculated from measurements of NiO-CdO and NiO-ZnO samples. Attention is attracted by the high value of Δ and its change of sign with a change in sample treatment temperature and also the abnormally low value of μ_B in comparison with $\mu = 2.8$ μ_B for Ni^{2+}. X-ray diffraction studies of the catalysts showed that at all firing temperatures the NiO-MgO catalysts were solid solutions, and even precision work in camera-monochromators with catalysts with a high NiO content failed to reveal line splitting, which would have indicated the presence of the free phase NiO. The results of measurement of the catalytic activity and the specific and total surface of the catalysts of the 750° series are given in Table 3 and Fig. 4. The data in Table 3 show that the main reaction was dehydrogenation of i-C_3H_7OH to acetone (98-99%); dehydration was insignificant and represented 0.5-2%; side processes of an oxidation–reduction nature, connected with the formation of CO and CO_2 were also insignificant (~1.0%). Pure MgO was characterized by a lower dehydrogenating capacity (~93%) and a higher dehydrating capacity (~6%) than binary catalysts. There was only 34% of dehydrogenation on pure NiO at 320 and 340° and the main process was cleavage with the formation of CO_2 and CH_4.

The activation energy E, calculated on the assumption that the reaction was first order, was 23 kcal/mole for MgO, which agrees with the value of E for pure MgO found by Roginskii et al. [10]. For all binary catalysts (2.3-36% of Ni) the activation energy was approximately constant and equaled 11 ± 2.5 kcal/mole. Evidently this fact also confirms the formation of solid solutions and the absence of free NiO or MgO phases. Figure 4 shows that the specific rate constant of dehydrogenation increased sharply with the addition of small amounts of NiO (2.34-4.6%), then fell somewhat, and again increased, beginning with 24% Ni (31% NiO). The surfaces of the catalysts were hardly changed with an increase in the NiO concentration and only in two cases (18.65 and 24.2% Ni) were they higher than for other samples, which may be connected with a mutual protection effect.

For catalysts fired at 400 and 600°, the activity was 1.5-3 times higher than for catalysts fired at 750°. However, for catalysts of this series we were unable to calculate E due to the insufficient reproducibility of the experiments, which was probably connected with the presence of small amounts of $NaNO_3$ in the catalysts. However, it should be noted that with an increase in firing temperature, the total catalyst activity fell in all cases. The binary catalyst with 36% Ni (46% NiO) fired at 400° at an experiment temperature of 360° showed a change in the mechanism of i-C_3H_7OH decomposition; the amount of saturated compounds reached 10% and the amount of CO_2 and CO reached 2%, which was apparently connected with reduction of NiO to Ni; this was also indicated by an increase in the susceptibility by a factor of 7 after operation and the appearance of dependence on field strength.

DISCUSSION OF EXPERIMENTAL RESULTS

The main problem which requires consideration in connection with the data obtained is the reason for the sharp increase in the catalytic activity of MgO in the dehydrogenation of i-C_3H_7OH when small amounts of NiO

TABLE 3

Sample No.	Amount of Ni in weight % (on NiO in MgO)	Catalyst activity						Gas composition					d in g/cc	s in m²/g	S_{total} in m²	E_{act} in kcal/mole
		320°		340°		360°		H_2	unsaturateds	CO_2	CO	saturateds				
		$k \cdot 10^4$	$k/s \cdot 10^4$	$k \cdot 10^4$	$k/s \cdot 10^4$	$k \cdot 10^4$	$k/s \cdot 10^4$									
1	MgO	10	0,21	15	0,32	37	0,79	93,3	5,6	0,8	0,3		0,468	50	47	22,8
2	2,34	41	0,98	58	1,38	105	2,50	98,0	1,7	0,3			0,462	46	42	11,5
3	4,60	91	1,90	131	2,72	178	3,70	97,5	2,0	0,5			0,463	52	48	11,9
4	6,00	85	1,85	116	2,52	175	3,80	97,2	2,3	0,5			0,472	50	46	11,4
5	10,40	75	1,53	101	2,06	170	3,46	99	0,5	0,4	0,3		0,509	48	49	14,2
6	18,65	129	1,43	156	1,73	248	2,75	98	1,3	0,5			0,563	80	90	10,4
7	24,20	89	1,16	113	1,46	210	2,72	98	1,5	0,7			0,559	71	80	13,7
8	29,60	130	2,06	158	2,50	223	3,53	98,1	1,2	0,7			0,696	46	63	8,7
9	36,00	168	2,27	253	3,41	479	6,47	97,8	1,0	0,6	0,6		0,704	53	74	14,8
10	NiO	—	—	—	—	—	—	34,3	—	16,1	3,5	46,1	2,393	—	—	—

are added. This fact cannot be explained by possible changes in the lattice parameters of the solid solution as the lattice parameters of MgO and NiO are very close (4.20 and 4.19 A, respectively). It seemed to us that in the given case the most probable explanation lies in the theory of semiconductors. In actual fact, a number of authors have shown [6, 11] that the introduction of small amounts of ions of different valence into the NiO lattice sharply changes the catalytic activity of NiO due to the appearance of Ni^{3+} ions. Analogous changes in catalytic activity may appear with the introduction of an n-semiconductor into a p-semiconductor and vice versa due to the sharp change in concentration of various defects. It is readily seen that in our case we do not have a change in valence of the ion Ni^{2+} (μ = 2.8-3.0 μ_B), and neither do we have semiconductors with different conductivity characteristics (MgO and NiO are p-semiconductors); therefore the above considerations cannot be applied directly to our case.

Nonetheless, the results we obtained may be explained quite satisfactorily if we apply Vol'kenshtein's theory [12] on the effect of the position of the Fermi level on the catalytic activity. MgO and NiO are actually p-semiconductors, but NiO has a higher p-conductivity than MgO. When NiO is introduced into MgO, Ni^{+2} ions will occupy acceptor levels of the system and due to the different p-character of NiO and MgO, there is the possibility of some transfer of electrons from the valence zone of MgO to Ni^{+2} ions. This transfer produces a fall in the Fermi potential and also an increase in the number of holes in MgO, which involves a larger number of i-C_3H_7OH molecules chemisorbed on the lattice defects (i-C_3H_7OH molecules act as electron donors) and leads to an increase in the reaction rate.

However, the fall in the Fermi potential, i.e., the transfer of electrons from the valence zone of MgO to acceptor levels, is limited to a comparatively small number of electrons which can undergo such a transfer. Therefore, the position of the Fermi potential reaches a minimum and correspondingly there is a maximum in the catalytic activity as is shown in Fig. 4. A further increase in NiO concentration produces no increase in activity as the transfer of electrons from the valence zone of MgO to acceptor levels stops and hence the Fermi potential no longer falls. The second increase in activity, beginning with 24.2% Ni, is explained by the accumulation of Ni^{+2} on the catalyst surface.

It might have been thought that the transfer of electrons from the valence zone of MgO to Ni^{2+} ions would change the magnetic moment of the Ni^{2+} ion. However, as Fig. 3 shows the magnetic moment is independent of NiO concentration. This is probably explained by the fact that the transfer of electrons is not great enough to produce an appreciable change in the magnetic moment with the present sensitivity of the method, but, nonetheless, it has a considerable effect on the catalytic activity. The increase in catalytic activity when small amounts of NiO are introduced indicates, in accordance

with the previous scheme, that the stage determining the reaction rate is the transfer of an electron from i-C_3H_7OH to the catalyst.

We made an attempt to demonstrate the transfer of electrons from the valence zone of the carrier to Ni^{2+} by magnetic methods. Samples of NiO-CdO and NiO-ZnO were prepared for this purpose. It is known that CdO and ZnO are n-semiconductors and with the introduction of Ni^{2+} ions into their lattice there is the possibility of the transfer of electrons to Ni^{2+}; the magnetic moment of this ion should change. Table 2 gives these results. This table shows that the magnetic moment (μ_B) for Ni^{2+} in both CdO and ZnO is much lower than the value 2.84 μ_B for Ni^{2+}. This is extremely interesting and indicates that here there is a strong transfer of electrons into the $\bar{d}$ shell of the Ni^{2+} ion with the formation of a d^9 configuration immediately or the initial formation of d^8s^1, with subsequent transition to d^9. This leads to a decrease in the number of unpaired electrons and consequently, a fall in the magnetic moment. The values of the Weiss constant for NiO-CdO and NiO-ZnO are large in comparison with the values for NiO-MgO at the same NiO concentrations, as is shown by the data in Table 2 and Fig. 3. One possible reason for this is strong Stark splitting under the effect of the electrical fields of ZnO and CdO.

The results of the present work show essential differences in the mechanism of the activating action of moderate additions of NiO to Al_2O_3 and MgO and the appearance of a specific activity maximum in both these cases; with NiO-Al_2O_3 the major role is played by "valence induction," while in the case of NiO-MgO these phenomena are connected with a change in the Fermi potential of the system. Here it should be remembered that NiO-Al_2O_3 is a dehydrating catalyst, while NiO-MgO is a dehydrogenating catalyst; in the first case the reaction is of the ionic type and in the second, the electronic type. Further investigations should show the extent to which the mechanisms discussed for the activating action of additives are characteristic of catalysts of these types.

SUMMARY

1. An investigation was made of the effect of the composition of coprecipitated NiO-MgO catalysts fired at 400, 600, and 750° on their magnetic and catalytic properties in the decomposition of i-C_3H_7OH.

2. The catalysts studied obeyed the Curie-Weiss law with the values of the Weiss constant increasing with the NiO content and a fall in sample firing temperature; the magnetic moment for all the samples was independent of NiO concentration and corresponded to the ion Ni^{2+} ($\mu = 2.8$-3.1 μ_B) within the limits of experimental error.

3. The specific catalytic (dehydrogenating) activity of preparations with small amounts of NiO added (up to 5 weight % of Ni) was much higher than that of pure MgO; a second increase in catalytic activity occurred at Ni > 24 weight % (~31% NiO) and is explained purely by the concentration factor.

4. The high activity of binary catalysts in the region of low NiO concentrations is explained on the basis of the semiconductor properties of NiO and MgO by the transfer of electrons from the valence zone of MgO to Ni^{2+}, which produces a corresponding fall in the Fermi potential. The possibility of such a transfer of electrons was demonstrated experimentally on the example of Ni-ZnO and NiO-CdO; the transfer of electrons of CdO and ZnO (p-semiconductors) to the Ni^{2+} ion led to a decrease in the magnetic moment of this ion.

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CHAIN-THERMAL FLAME PROPAGATION

COMMUNICATION 3. EFFECT OF DIFFUSION COEFFICIENT AND THERMAL CONDUCTIVITY

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In the first article [1], chain-thermal flame propagation was examined with a simplified scheme for the chain reaction, the mathematical description of which gives a system of differential equations for diffusion of the active center and heat conductivity. The rate of heat evolution in the reaction zone of a laminar flame depends on the interaction of the thermal and diffusion currents and is largely determined by the diffusion of active centers from the flame region with a high concentration of them, and a high temperature [1]. In the present article a relation was obtained connecting the rate of flame propagation with the diffusion coefficient of the leading active center, heat conductivity, and other kinetic and thermodynamic values for the given fuel mixture.

Derivation of relation. According to article [1], for the rate of flame propagation u_0 it is possible to obtain the relation

$$u_0 = \frac{1}{\rho_0}\, \eta_i \rho_*,\tag{1}$$

where

$$\eta = \frac{4D_0}{\varkappa T_m}, \quad \varkappa = \frac{cD_0}{\lambda_0}\, \text{and}\, D = \rho D_p;$$

$$p_*^2 = \frac{(\gamma - \beta\eta_i) + \sqrt{(\gamma - \beta\eta)^2 + 4\delta\eta_i\alpha}}{2\eta_i\alpha};$$

$$\alpha = 2D_m \frac{c}{Q_m}, \quad \beta = \frac{n}{2}\frac{C}{C}T_m, \quad \gamma = D_m n_C \quad \delta = R_m T_m^2, \quad Q_m = h n_{Am} K_m,\tag{2}$$

$$K_m = Z_A \frac{1}{\mu_P}\, \rho_m^2 \exp(-E/RT_m'), \quad R_m = Z_B \frac{\mu_P}{\mu_A}\, \rho_m n_{Am} \exp(-E_P/RT_m'),$$

$$\rho_m = \rho_0 \frac{\mu_m}{\mu_0}\frac{T_0'}{T_m'}, \quad T_m' = \frac{T_C' + T_0'}{2}, \quad T_m = \frac{T_C' - T_0'}{2},$$

where ρ_0 is the mixture density at the initial temperature T_0' °K, n_C is the dimensionless weight concentration of the active center at the combustion temperature $T_C' = T_C + T_0'$, $\underline{c}$ is the heat capacity, D_p is the diffusion coefficient of the active center, n_A is the starting material concentration, $\underline{h}$ is the heat effect of the reaction, K_m is the rate constant of the reaction at temperature T_m' °K, corresponding to the maximum value of the temperature

gradient, R_m is the rate of generation of the active center at temperature T'_m. μ_P is the molecular weight of the active center, μ_A is the molecular weight of the starting material, and μ is the apparent molecular weight of the mixture. The index "0" refers to the initial state and the index "C" to the state at the combustion temperature T'_C.

Assuming that the temperature dependence of the diffusion coefficient has the form $D_P \sim (T')^a$, with $q = \mu_0/\mu_m (T'_0/T'_m)^{a-1}$:

$$D_0 = D_m q, \quad \eta = 4 D_m q \frac{1}{\varkappa T_m}. \tag{3}$$

From (1), considering (2) and (3), we find a relation for determining the flame propagation rate

$$u_0 = \varphi \xi \frac{1}{\rho_0} \sqrt{\frac{n_C Q_m (\rho D_\nu)_m}{2 c T_C}} = \varphi \xi \frac{1}{2 \rho_0} \sqrt{n_C K_m \rho_m D_{Pm}}, \tag{4}$$

where

$$\varphi = 2 \sqrt{\frac{2q}{\varkappa} \left(1 - \frac{2q}{\varkappa}\right)}, \tag{5}$$

$$\xi = \sqrt{\frac{1}{2} (1 + \sqrt{1 + M})}, \tag{6}$$

$$M = \frac{4 \delta \eta \alpha}{(\gamma - \beta \eta)^2} = \frac{32 q \varkappa}{(\varkappa - 2q)^2} \frac{R_m}{K_m n_C^2}. \tag{7}$$

By using the index "H" to denote values in the initial state and the index "L" for values in the new state, we obtain from (4) a relation for the ratio of the flame propagation rates:

$$\frac{u_{0L}}{u_{0H}} = \frac{\varphi_L \xi_L}{\varphi_H \xi_H} G_T \sqrt{\frac{(n_C \rho_C)_L (D_\nu)_{0L}}{(n_C \rho_C)_H (D_\nu)_{0H}}} \exp\left[\frac{E}{R}\left(\frac{1}{T'_{CH} + T'_{0H}} - \frac{1}{T'_{CL} + T'_{0L}}\right)\right], \tag{8}$$

where

$$G_T = \sqrt{\frac{\mu_{mL}^3 u_{CH} \mu_{0H}^2}{\mu_{CH} \mu_0^2 u_{mH}^3}} \sqrt{\frac{Z_{AL} T'_{CL} (T'_{01})^{2-a} (T'_{CH} + T'_{0H})^{3-a}}{Z_{AH} T'_{CH} (T'_{0H})^{2-a} (T'_{CL} + T'_{0L})^{3-a}}}. \tag{9}$$

The relation (8) makes it possible to calculate the ratio of the flame propagation rates with a change in the diffusion coefficient and heat conductivity, and also to find the dependence of u_0 on pressure and temperature without calculating the absolute values of the propagation rates.

The dependence of u_0 on the ratio of the diffusion coefficient of the active center to the thermal conductivity coefficient $\kappa = c\rho D_P/\lambda$ according to (4) is expressed through φ and ξ. In the cases where it is permissible to neglect the rate of generation of active centers, i.e., to assume that $R_m = 0$, $\xi = 1$, the whole dependence of u_0 on κ is determined solely by the coefficient φ, which is independent of the rate constants of the chemical reactions. A decrease in κ, i.e., an increase in the thermal conductivity λ or a decrease in the diffusion coefficient D_P, under otherwise equal conditions, produces an increase in the coefficient ξ (6). This is caused by the fact that in this case there is a relative decrease in the number of active centers reaching the reaction zone by diffusion, and consequently there is a relative increase in the role of the rate of generation of active centers. Therefore, an increase in the thermal conductivity with the diffusion-coefficient constant may on the whole have a different effect on the flame propagation rate, depending on the ratio of the values in formula (7) for M. This value will be greater, the greater the generation rate and the smaller n_C, as the diffusion current of the active center depends on the value of n_C. Normally, the rate of generation of active
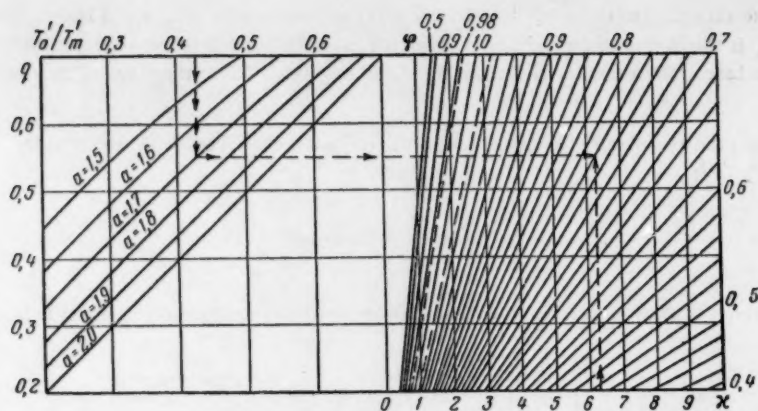
Fig. 1. Nomogram for determining the coefficient φ in relation to κ and $T_0'T_m'$ at various values of the index $\underline{a}$.
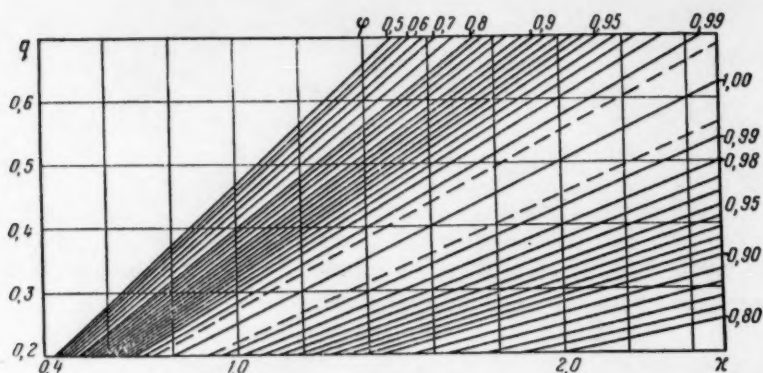
Fig. 2. Right-hand part of nomogram from Fig. 1 (on a larger scale).

centers is low and M will be less than unity while ($\kappa - 2q$) will be of the order of unity. This is explained by the fact that the activation energy of the generation rate $E_P \gg E$ and approximately equals the heat of formation of the active center, determining the value of the equilibrium constant from which n_C is calculated. However, in the case of a branched chain reaction, the effect of M may be more appreciable. The rate of chain branching may be represented as $iK_m n_{Am} n_m$ [1], where $\underline{i}$ is the chain-branching coefficient. Now the rate of chain branching for [7] is conditionally represented as the rate of chain generation, assuming that $R_m' = R_m +$ + $iK_m n_{Am} n_m$. Then $M' = M + \Delta M$, where

$$\Delta M = \frac{32q\kappa}{(\kappa - 2q)^2} \frac{iK_m n_{Am} n_m}{K_m n_C^2} \approx \frac{32q\kappa}{(\kappa - 2q)^2} \frac{n_{Am}}{2n_C} i.$$

Now it is evident that at the beginning of chain branching, the coefficient ξ will depend mainly on the rate of chain branching (at not very small values of $\underline{i}$). Therefore, with an increase in the rate of chain branching (an increase in $\underline{i}$), a change in thermal conductivity will have a more considerable effect on the change in flame propagation rate due to the more considerable increase or decrease in the value of the coefficient ξ according to Eqs. (6) and (7).

Figure 1 gives a nomogram for determining the coefficient φ in relation to κ and T_0'/T_m' at various values of the index $\underline{a}$ [the values of $q = (T_0'/T_m')^{a-1}$ are plotted along the vertical axis at the left]. Figure 2 gives the right-hand part of the nomogram from Fig. 1 on a larger scale. The data presented in Figs. 1 and 2 show that

TABLE

Ratio of Flame Propagation Rates in Methane − Oxygen Mixtures with Nitrogen (Air Mixture), Argon, and Helium with 9.46% Methane

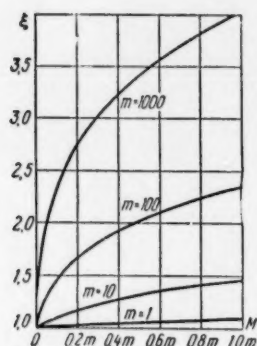| Source	$(u_0)_{N_2}$	$(u_0)_A$	$(u_0)_{He}$
Experimental data [2]	0.43	1	1.42
From thermal theory [2]	−	1	2.03
From theory of Tanford and Pease [2]	0.36	1	1.32
From relation (8) for H atoms	0.31	1	1.77
From relation (8) for OH	0.43	1	0.91

Fig. 3. Relation of the coefficient ξ from Eq. (6) to the value of M.

the effect of the value of κ on the flame propagation rate may vary, depending on the ratio of the temperatures T_0'/T_m' and the index a. Figure 3 gives the relation of the coefficient ξ to the value of M according to Eq. (6).

Numerical calculations. Relation (8) obtained was applied to the calculation of the ratio of flame propagation rates in three stoichiometric methane−oxygen mixtures (9.46% methane), containing identical amounts of different inert diluents: a mixture with nitrogen (air mixture),a mixture with argon instead of nitrogen, and a mixture with helium instead of nitrogen. Without considering the detailed mechanism of the chemical conversion, we will assume that the form of the rate constant of heat evolution K remains the same with a change in the inert diluent and that the heat evolution rate is determined mainly by the diffusion of one of the active centers for which the product of the diffusion coefficient and its concentration at the combustion temperature T_C' will be greater.

The experimental ratio of the flame propagation rates for these three mixtures $(u_0)_{N_2} : (u_0)_A : (u_0)_{He}$ was given in the work of Clingman, Brokaw, and Pease [2] (table). The value of the flame propagation rate in the methane−oxygen mixture plus argon in the table was taken as unity; $(u_0)_A = 1$. All the data necessary for calculations from relation (8) were taken from [2]. The value of the activation energy E = 13.7 kcal/mole, which appears in (8), was determined by means of relation (8) from the pressure dependence of u_0 in a stoichiometric methane−oxygen mixture [3]. For the index a we took the value a = 1.9. The ratio of the flame propagation rates from (8) was calculated from the concentrations and diffusion coefficients of hydrogen atoms and hydroxyl (table).

It is possible that the value of the diffusion coefficient of OH in a mixture with helium presented in [2] is somewhat low. In view of the fact that in comparison with the concentration of H atoms, the concentration of hydroxyl is high at the combustion temperature for 9.46% methane in mixtures with argon or helium, the ratio $(u_0)_A : (u_0)_{He}$ apparently must be determined mainly by the concentrations and diffusion coefficients of hydroxyl and not H atoms. Therefore, a more accurate determination of the diffusion coefficients of hydroxyl, which is beyond the scope of the present article, is extremely important.

It is possible that to refine the theoretical ratios of the flame propagation rates it is necessary to consider the branching rate (in the present calculations considering generation, it was established that in all cases $\xi = 1$ and therefore it is possible to neglect the chain generation rate in the calculation of the ratios in the table). The reason for the insufficiently close agreement between the ratio calculated on OH and the experimental value may be the fact that the theoretical relation (8) was obtained for a simplified scheme for the chain reaction, allowing for diffusion of only one active center. Further refinement of the theoretical relations for determining the dependence of flame propagation rate on thermal conductivity and diffusion coefficients will be carried out after publication of the theory of flame propagation, allowing for the diffusion of two active centers.

SUMMARY

An equation was derived relating the flame propagation rate to the diffusion coefficient of the leading active center and the thermal conductivity; it was used to calculate the ratio of the flame propagation rates

in three methane—oxygen mixtures containing nitrogen (air mixture), argon instead of nitrogen, and helium instead of nitrogen. The theoretical ratios of the propagation rates were in agreement with experimental ratios.

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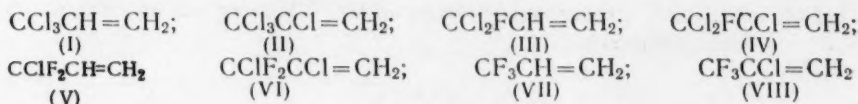* Original Russian pagination. See C. B. Translation.

PREPARATION OF SOME CHLORO FLUORO DERIVATIVES
FROM 1,1,1,3-TETRACHLOROPROPANE

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As two of the authors of the present paper showed in collaboration with Firstov [1], various polychloro derivatives of propane and propene can be obtained from 1,1,1,3-tetrachloropropane by successive reactions of dehydrochlorination and chlorination. The resulting compounds can be used in the synthesis of chloro fluoro derivatives of propane and propene [2, 3]. Thus, Haszeldine [3] described the preparation of chloro fluoro olefins of the types $CF_3CX=CH_2$ and $CF_2ClCX=CH_2$, in which X = H, Cl, or Br, by the fluorination of the compounds described in the above-mentioned paper [1].

We considered it to be of interest to prepare also compounds of the type $CCl_2FCX=CH_2$, in which X = H or Cl, for the purpose, in particular, of making a comparative study of the tendency of the following halopropenes to undergo allyl rearrangement:

$$CCl_3CH=CH_2; \quad CCl_3CCl=CH_2; \quad CCl_2FCH=CH_2; \quad CCl_2FCCl=CH_2;$$
$$\text{(I)} \qquad\qquad \text{(II)} \qquad\qquad \text{(III)} \qquad\qquad \text{(IV)}$$
$$CClF_2CH=CH_2 \quad CClF_2CCl=CH_2; \quad CF_3CH=CH_2; \quad CF_3CCl=CH_2$$
$$\text{(V)} \qquad\qquad \text{(VI)} \qquad\qquad \text{(VII)} \qquad\qquad \text{(VIII)}$$

It was also of interest to prepare chloro fluoro derivatives containing reactive groups from 1,1,1,3-tetrachloropropane. These chloro fluoro olefins were obtained by us as follows:

$$CCl_3CHXCH_2Cl \xrightarrow[\text{Sb Cl}_5]{SbF_3}
\begin{cases}
\longrightarrow CCl_2FCHXCH_2Cl \rightarrow CCl_2FCX=CH_2 \\
\qquad\qquad \text{(IX)} \\
\longrightarrow CClF_2CHXCH_2Cl \rightarrow CClF_2CX=CH_2 \\
\qquad\qquad \text{(X)} \qquad\qquad\quad \downarrow \\
\qquad\qquad\qquad\qquad\qquad CF_3CX=CH_3
\end{cases}$$
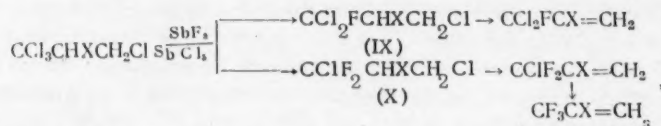
in which X = H or Cl.

The structures of the monofluoro compounds (III), (IV), and (IX) were proved by their conversion into the known difluoro compounds (V), (VI), and (X) under the action of antimony trifluoride in presence of antimony pentachloride.

The investigation showed that the tendency to undergo allyl rearrangement falls in the series $CCl_3CR = CH_2$, $CCl_2FCR = CH_2$, and $CClF_2CR = CH_2$, in which R = H or Cl. Whereas $CCl_3CH = CH_2$ and $CCl_3CCl = CH_2$ are completely isomerized when heated to 150° [1], the compounds $CClF_2CH = CH_2$ and $CClF_2CCl = CH_2$ have almost no tendency to undergo allyl rearrangement under these conditions. The corresponding monofluoro compounds occupy an intermediate position in this respect.

As already reported [1], 3,3,3-trichloropropene and 2,3,3,3-tetrachloropropene condense with benzene in presence of a little $AlCl_3$ even at room temperature; the products have the structures $C_6H_5CH_2CH=CCl_2$ and $C_6H_5CH_2CCl=CCl_2$, respectively, which indicates the occurrence of allyl rearrangement in the course of these reactions. It was of interest to compare the behavior of 2,3-dichloro-3,3-difluoropropene under these conditions. It was found that in this case reaction proceeds only with difficulty, it being necessary to heat and to keep on adding new portions of $AlCl_3$. It was found that the product was not a monochloro difluoro derivative, as would be expected, but the dichloro monofluoro derivative $C_6H_5CH_2CCl=CClF$. The structure of this compound was proved by its oxidation with alkaline potassium permanganate solution with formation of phenylacetic acid.

The low probability that reaction occurs with allyl rearrangement at the expense of a fluorine atom compels us to suppose that in this case aluminum chloride and benzene act simultaneously on the difluoro compound, which may be expressed by the scheme:

$$AlCl_3 \quad F—CPCl—Cl=CH_2 \quad H—C_6H_5$$
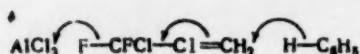
The reaction of 3,3-dichloro-3-fluoropropene with benzene and aluminum chloride proceeds analogously with formation of 1,1-dichloro-3-phenylpropene. In connection with this unusual course of reaction at the expense of a fluorine atom, we studied the action of cuprous cyanide on 3,3-dichloro-3-fluoropropene. We have shown previously [4] that on reaction with cuprous cyanide 3,3,3-trichloropropene is converted into 4,4-dichloro-3-butenenitrile.

The reaction of cuprous cyanide with 3,3-dichloro-3-fluoropropene is analogous to that with 3,3,3-trichloropropene and proceeds at the expense of a chlorine atom and with allyl rearrangement with formation of 4-chloro-4-fluoro-3-butenenitrile. The structure of the nitrile was proved by hydrolysis to succinic acid in a medium of concentrated sulfuric acid. 3-Chloro-3,3-difluoropropene reacts with cuprous cyanide only under severe conditions at about 250° with formation of a mixture of products, from which small yields were isolated of 4,4-difluoro-3-butenenitrile and of a compound of composition $C_4H_4NF_3$, which was probably trifluorobutyronitrile. The formation of the latter compound shows that the reaction is complicated and is probably accompanied by the liberation of hydrogen fluoride.

Hydrolysis of 4-chloro-4-fluoro-3-butenenitrile with a mixture of hydrochloric and acetic acids gave 4-chloro-4-fluoro-3-butenoic acid, which was characterized as its anilide. By the action of chlorine on 4-chloro-4-fluoro-3-butenenitrile we obtained 3,4,4-trichloro-4-fluorobutyronitrile. Hydrolysis of this nitrile gave 3,4,4-trichloro-4-fluorobutyric acid, which was characterized as its anilide. The same acid was obtained by the action of chlorine on 4-chloro-4-fluoro-3-butenoic acid.

EXPERIMENTAL

Preparation of $CClF_2CH_2CH_2Cl$ and $CCl_2FCH_2CH_2Cl$. A mixture of 210 g (1.13 moles) of 1,1,1,3-tetrachloropropane, 180 g (1 mole) of antimony trifluoride, and 18 g of antimony pentachloride was heated in an oil bath in a flask having a long vertical tube connected with a condenser set for distillation. The reaction started at 120°, and at first the difluoro compound distilled off, and then, at a higher temperature, the monofluoro compound. A considerable amount of hydrogen chloride was also liberated. The distillate was washed with hydrochloric acid and then with water; it was dried over calcium chloride. Fractionation through a 40 cm Vigreux column gave 88 g (51%) of 1,3-dichloro-1,1-difluoropropane and 20 g (10%) of 1,1,3-trichloro-1-fluoropropane. 1,3-Dichloro-1,1-difluoropropane has b. p. 80.5-81°; $n^{20}D$ 1.3792; d^{20}_4 1.3520; found MR 25.48. $C_3H_4Cl_2F_2$. calculated MR 25.58. For this substance the literature [3] gives: b. p. 81-81.5°; $n^{20}D$ 1.3775; d^{20}_4 1.339. 1,1,3-Trichloro-1-fluoropropane has b. p. 118-118.5°; $n^{20}D$ 1.4302; d^{20}_4 1.4055; found MR 30.50. $C_3H_4Cl_3F$. calculated MR 30.55. Found: Cl 64.72; 64.62%. Calculated: Cl 64.40%.

3,3-Dichloro-3-fluoropropene. A solution of 15 g (0.27 mole) of potassium hydroxide in 30 ml of alcohol was added gradually at room temperature with stirring to 30 g (0.18 mole) of 1,1,3-trichloro-1-fluoropropane. After three hours the reaction mixture was diluted with water, and the oil formed was separated and dried over calcium chloride. Distillation gave 19.7 g (84%) of 3,3-dichloro-3-fluoropropene; b. p. 57.5-58°; $n^{20}D$ 1.4018; d^{20}_4 1.2401; found MR 25.24. $C_3H_3Cl_2FF$. calculated MR 25.32. Found: Cl 55.31; 55.39%. Calculated: Cl 55.04%.

Preparation of $CClF_2CHClCH_2Cl$ and $CCl_2FCHClCH_2Cl$. A mixture of 125 g (0.58 mole) of 1,1,1,2,3-pentachloropropane, 90 g (0.50 mole) of antimony trifluoride, and 5 g of antimony pentachloride was prepared in a round-bottomed flask fitted with a vertical tube (40 cm) connected with a condenser. The mixture was heated over a naked flame so that rapid distillation occurred. The product was collected under a layer of hydrochloric acid, and was then carefully washed with hydrochloric acid and with water and was dried over calcium chloride. The produce was distilled with collection of the following fractions: Fraction I (up to 113°), 1 g; Fraction II (113-140°), 32.5 g; Fraction III (140-170°), 29.5 g; residue, 6 g.

Two distillations of Fraction II gave 29.5 g (28%) of the difluoro compound; b. p. 113.4-114.5°; $n^{23}D$ 1.4126. According to Haszeldine [3]: b. p. 113°; $n^{20}D$ 1.415.

From Fraction III we isolated the monofluoro compound, yield 21 g (18%); b. p. 154-155°; $n^{20}D$ 1.4669; d^{20}_4 1.5610; found MR 35.51. $C_3H_3Cl_4F$. calculated MR 35.42. Found: C 18.14; 18.39; H 1.50; 1.49; Cl 70.42; 70.12%. Calculated: C 18.02; H 1.52; Cl 70.95%.

By variation of the amount of $SbCl_5$ either the monofluoro compound or the difluoro compound can be obtained as the main product.

2,3,3-Trichloro-3-fluoropropene. The reaction was carried out as described for the preparation of 3,3-dichloro-3-fluoropropene. From 32 g of $CCl_2FCHClCH_2Cl$ and 14 g of KOH in 35 ml of alcohol we obtained 15.5 g (59.4%) of product, which after two distillations had: b. p. 98.5-98.7° (742 mm); $n^{20}D$ 1.4402; d^{20}_4 1.4353; found MR 30.02. $C_3H_2Cl_3FF$. calculated MR 30.08. Found: Cl 64.44; 64.20%. Calculated: Cl 65.09%.

Allyl rearrangement of 3,3,3-trichloropropene when heated with antimony trifluoride. A mixture of 12 g (0.088 mole) of 3,3,3-trichloropropene (b. p. 101°) and 18 g (0.10 mole) of SbF_3 was heated for two hours at 140-150° in a stainless-steel test tube. This gave 11 g of a substance of b. p. 131-131.5°, identical in all its properties to 1,1,3-trichloropropene; no products of the replacement of chlorine by fluorine were found.

Allyl rearrangement of $CCl_3CCl=CH_2$ under the action of antimony pentachloride. The tetrachloropropene (24 g) was cooled to 0°, and 1.1 g of antimony pentachloride was added. The mixture was left overnight at room temperature. The reaction product was washed with hydrochloric acid and with water, and was dried over calcium chloride. Distillation gave 20 g of an isomeric tetrachloropropene, $CCl_2=CCl-CH_2Cl$, which after two distillations had: b. p. 165.5-166.5° (766 mm); $n^{20}D$ 1.5198.

Allyl rearrangement of 3,3-dichloro-3-fluoropropene when heated with antimony trifluoride. A mixture of 11.5 g (0.09 mole) of the dichlorofluoropropene (b. p. 58°) and 15 g (0.083 mole) of SbF_3 was heated for three hours at 150-155° in a steel test tube. The reaction mixture was treated with dilute hydrochloric acid. The oil was separated and dried over calcium chloride. Fractionation gave 4.6 g of 1,3-dichloro-1-fluoropropene; b. p. 88.6-89.3°; $n^{20}D$ 1.4310; d^{20}_4 1.3186; found MR 25.32. $C_3H_3Cl_2FF$. calculated MR 25.32.

Behavior of 3-chloro-3,3-difluoropropene when heated with antimony trifluoride. A mixture of 12 g (0.11 mole) of 3-chloro-3,3-difluoropropene and 10 g (0.06 mole) of antimony trifluoride was heated for four hours at 160-180° in a steel test tube. We recovered 11 g of unchanged 3-chloro-3,3-difluoropropene, b. p. 21-22°. In presence of a little $SbCl_5$ fluorination went smoothly with formation of 3,3,3-trifluoropropene.

Behavior of 2,3,3-trichloro-3-fluoropropene when heated with antimony trifluoride. A mixture of 13.1 g (0.08 mole) of 2,3,3-trichloro-3-fluoropropene and 18 g (0.1 mole) of SbF_3 was heated for four hours at 160-180° in a steel test tube. We recovered 10.8 g of unchanged 2,3,3-trichloro-3-fluoropropene; b. p. 98-99°; $n^{20}D$ 1.4402.

Behavior of 2,3-dichloro-3,3-difluoropropene when heated with antimony trifluoride. When 14.7 g (0.1 mole) of 2,3-dichloro-3,3-difluoropropene was heated with 12 g of antimony trifluoride at 170-180° for four hours, no reaction occurred: we isolated 13 g of unchanged 2,3-dichloro-3,3-difluoropropene; b. p. 54-55°; $n^{20}D$ 1.3770. In presence of a little antimony pentachloride fluorination went smoothly with formation of 2-chloro-3,3,3-trifluoropropene.

Reaction of 2,3-dichloro-3,3-difluoropropene with benzene and aluminum chloride. Aluminum chloride (0.5 g) was added to a solution of 12 g (0.082 mole) of the dichlorodifluoropropene in 50 ml of benzene, and the mixture was boiled in a water bath for four hours. From time to time (when the liberation of HCl ceased) more aluminum chloride was added (altogether, 3 g, i.e., 0.023 mole, was added). The mixture was poured

into water. The oily layer was washed with hydrochloric acid and with water, and was dried over calcium chloride. Benzene was distilled off, and in the vacuum distillation of the residue 13.2 g (78.6%) of a fraction of b. p. 86-89° (6 mm) was collected. After further distillation the substance had: b. p. 84-84.5° (5.5 mm); $n^{20}D$ 1.5256; d^{20}_4 1.2759; found MR 49.30. $C_9H_7Cl_2FF$, calculated MR 49.32. Found: C 52.63; 52.42; H 3.58; 3.33; Cl 34.32; 34.31%. Calculated: C 52.71; H 3.44; Cl 34.58%.

Reaction of 3,3-dichloro-3-fluoropropene with benzene and aluminum chloride. Aluminum chloride (2 g) was added in portions to a solution of 10 g of 3,3-dichloro-3-fluoropropene in 50 ml of benzene. The mixture was heated in a water bath until the liberation of hydrogen chloride ceased. The solution was washed with water and dried over calcium chloride. Benzene was distilled off, and the residue was vacuum-distilled. This gave 9.1 g of 1,1-dichloro-3-phenylpropene; b. p. 95-95.5° (6.5 mm); $n^{20}D$ 1.5495; d^{20}_4 1.2022; found MR 49.53; calculated MR 49.43. The following constants are known [1] for this substance: b. p. 94-95° (6 mm); $n^{20}D$ 1.5490; d^{20}_4 1.2032.

4-Chloro-4-fluoro-3-butenenitrile. A mixture of 12.9 g of 3,3-dichloro-3-fluoropropene and 10 g of cuprous cyanide was heated for 2.5 hours at 160-170° in a steel test tube. The reaction product was distilled off. Two distillations gave 6 g (50.4%) of 4-chloro-4-fluoro-3-butenenitrile; b. p. 61-62° (21 mm); $n^{20}D$ 1.4279; d^{20}_4 1.2419; found MR 24.76. C_4H_3ClFN, calculated MR 24.79. Found: Cl 29.05, 29.03%. Calculated: Cl 29.66%. Hydrolysis of the nitrile (0.5 g) in 10 ml of 92% sulfuric acid at 120° gave 0.3 g of succinic acid, which showed no depression of melting point in admixture with known succinic acid.

4-Chloro-4-fluoro-3-butenoic acid. A solution of 6 g of 4-chloro-4-fluoro-3-butenenitrile in a mixture of 10 ml of acetic acid, 6 ml of hydrochloric acid, and 6 ml of water was boiled for eight hours. The mixture was diluted with water and extracted with ether. Solvent was distilled off, and two distillations gave 5.9 g (85%) of 4-chloro-4-fluoro-3-butenoic acid; b. p. 95-96° (10 mm); $n^{20}D$ 1.4397; d^{20}_4 1.3720, found MR 26.59. $C_4H_4ClFO_2$, calculated MR 26.51. The anilide has m. p. 75-76° (from a mixture of benzene and petroleum ether). Found: N 6.56; 6.64%. $C_{10}H_9ClFNO$. Calculated: N 6.56%.

3,4,4-Trichloro-4-fluorobutyric acid. Chlorine was passed to saturation through an illuminated, boiling solution of 4 g of 4-chloro-4-fluoro-3-butenoic acid in 10 ml of carbon tetrachloride. Solvent was distilled off, and the residue was vacuum-distilled. Redistillation gave 5.5 g (90%) of 3,4,4-trichloro-4-fluorobutyric acid; b. p. 121° (8 mm); $n^{20}D$ 1.4654; d^{20}_4 1.5756; found MR 36.77. $C_4H_4Cl_3FO_2$, calculated MR 36.71. On standing the acid solidified; m. p. 29-30° (from petroleum ether). Found: C 23.05; 23.03; H 2.12; 2.15%. Calculated: C 22.94; H 1.92%. Heating of the acid with thionyl chloride gave the acid chloride ($CFCl_2CHClCOCl$); b. p. 62-63° (8 mm); $n^{20}D$ 1.4700. The anilide has m. p. 123-124° (from benzene and petroleum ether). Found: N 5.13; 5.16%. Calculated: N 4.92%.

3,4,4-Trichloro-4-fluorobutyronitrile. The procedure was as in the preceding experiment. The chlorina- of 5 g of 4-chloro-4-fluoro-3-butenenitrile gave 7.1 g of 3,4,4-trichloro-4-fluorobutyronitrile; b. p. 87-88° (8 mm); $n^{20}D$ 1.4641; d^{20}_4 1.5052; found MR 34.92. $C_4H_3Cl_3FN$, calculated MR 34.99. Found: C 25.36; 25.34; H 1.77; 1.81; Cl 56.19; 56.47%. Calculated: C 25.22; H 1.56; Cl 55.86%. Hydrolysis of the nitrile in a mixture of hydrochloric and acetic acids gave 3,4,4-trichloro-4-fluorobutyric acid, which was identified as its anilide.

Action of cuprous cyanide on 3-chloro-3,3-difluoropropene. A mixture of 10 g of 3-chloro-3,3-difluoropropene and 10 g of cuprous cyanide was heated for two hours at 250° in a steel test tube. The reaction product was fractionated. Repeated fractionation gave 2 g of a fraction of b. p. 122-124°, and this consisted mainly of 4,4-difluoro-3-butenenitrile. Found: F 35.24; 35.95%. $C_4H_3F_2N$. Calculated: F 36.87%. Hydrolysis of this fraction with concentrated sulfuric acid gave succinic acid in 50% yield. We obtained also 2 g of a substance having: b. p. 139-140°; $n^{20}D$ 1.3421; d^{20}_4 1.2484; Found MR 20.77. $C_4H_4F_3N$. Calculated MR 20.18. Found: C 39.09; 39.08; H 3.35; 3.39; N 11.33; 11.54%. Calculated: C 39.03; H 3.28; N 11.38%. This appeared to be trifluorobutyronitrile.

SUMMARY

1. A study was made of the possibility of the occurrence of allyl rearrangement and exchange reactions in compounds of structures:

$$CCl_3CH=CH_2 \qquad CCl_3CCl=CH_2$$
$$CCl_2FCH=CH_2 \qquad CCl_2FCCl=CH_2$$
$$CClF_2CH=CH_2 \qquad CClF_2CCl=CH_2$$
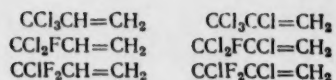
when heated with antimony trifluoride. As the number of fluorines in the trihalomethyl group increases, the tendency for these compounds to undergo isomerization falls.

2. The condensation of 3,3-dichloro-3-fluoropropene and of 2,3-dichloro-3,3-difluoropropene with benzene in presence of aluminum chloride proceeds with allyl rearrangement and the loss of one atom of fluorine.

3. Reaction of 3,3-dichloro-3-fluoropropene and of 3-chloro-3,3-difluoropropene with cuprous cyanide proceeds with allyl rearrangement and the loss of one atom of chlorine.

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DIENE CONDENSATION OF UNSATURATED COMPOUNDS CONTAINING
THE TRICHLOROMETHYL OR TRICHLOROVINYL GROUP

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The reactions of nucleophilic reagents with 3,3,3-trichloropropene proceed with transfer of the reaction center, which may be illustrated by the scheme [1, 2]:

$$X^\ominus + CH_2{=}CH{-}C{<}^{Cl}_{Cl}{-}Cl \longrightarrow X{-}CH_2CH{=}CCl_2 + Cl^\ominus,$$
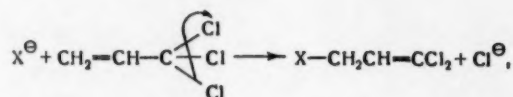
where $X^\ominus{=}CN^\ominus$, $I^\ominus$, $CH_3COO^\ominus$, etc.

It was of interest to study the behavior of 3,3,3-trichloropropene in the diene synthesis: it is known that not only 1,3-dienes, but also systems containing π-σ conjugation, will undergo diene condensation [3]. The following reactions may be expected with, for example, cyclopentadiene:

a) the usual diene synthesis

(I)
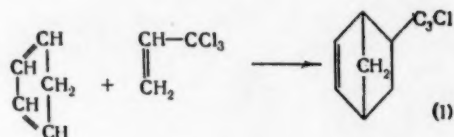
b) diene synthesis in which 3,3,3-trichloropropene takes part as a π-σ conjugated system

(II)
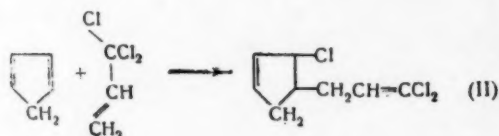
c) preliminary isomerization of 3,3,3-trichloropropene into 1,1,3-trichloropropene with subsequent reaction with the diene by the scheme of the usual diene synthesis
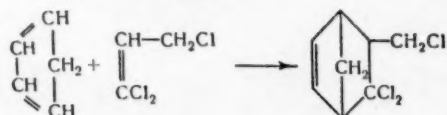
Study of the last possibility is all the more interesting in that the extent to which the accumulation of halogen atoms at the double bond lowers the reactivity of alkenes and alkadienes in the diene synthesis is still obscure. Trichloroethylene does not react with butadiene [4]. With tetraphenylcyclopentadienone [5] and with cyclopentadiene [6] it gives anomalous products, and only with anthracene [4] does it form a normal adduct. Tetrachloroethylene has not been caused to undergo diene condensation [4].

Halobutadienes of the type $CH_2=CR-CX=CHX$, in which R = H, CH_3, or Cl and X = Cl or Br, do not undergo diene condensation with maleic anhydride [7, 8]; only 1,4-dichloro-1,3-butadiene reacts with maleic anhydride according to the Diels-Alder scheme [9]. The possibility of using unsaturated compounds of this type as dienophilic substances has not been investigated. In this connection we have studied the behavior in the Diels-Alder reaction of the recently synthesized [10] 1,1,2-trichloro-1,3-butadiene, which contains a trichlorovinyl and a vinyl group in the same molecule.

It was found that 3,3,3-trichloropropene reacts with cyclopentadiene at 180-200° with formation of 5-(trichloromethyl)bicyclo[2.2.1]hept-2-ene. This adduct does not condense further with cyclopentadiene when heated at 180-200° for six hours in a sealed tube. The adduct formed by 3,3,3-trichloropropene with cyclopentadiene remains unchanged when boiled for ten hours with sodium iodide in acetone; it therefore does not contain a chlorine atom that can be replaced by iodine, and it cannot have the structure (II). Also, the compound obtained by the dehydrochlorination of the product of the reaction of 3,3,3-trichloropropene with cyclopentadiene combines with only one equivalent of mercuric acetate and therefore contains only one −CH=CH− grouping in the molecule;*such a compound can be formed only from (I) and must have the structure 5-(dichloromethylene)bicyclo[2.2.1]hept-2-ene. Scheme (c) must also be rejected because 1,1,3-trichloropropene could not be caused to undergo diene condensation with cyclopentadiene, isoprene, or butadiene. By these reactions the structure of the adduct formed by 3,3,3-trichloropropene with cyclopentadiene as 5-(trichloromethyl)bicyclo[2.2.1]hept-2-ene is confirmed fairly unequivocally. 5-(Trichloromethyl)bicyclo[2.2.1]hept-2-ene was reduced over a platinum catalyst to 2-(trichloromethyl)norcamphane, i.e., 2-(trichloromethyl)bicyclo[2.2.1]heptane, and it was also converted into a crystalline vicinal chloromercuri methoxy derivative by the action of mercuric acetate in methanol with treatment of the reaction product with sodium chloride solution.

When heated with 92% sulfuric acid, 5-(trichloromethyl)bicyclo[2.2.1]hept-2-ene and 2-(trichloromethyl)-norcamphane are resinified without formation of the corresponding acids. Nitric acid of sp. gr. 1.513 vigorously oxidizes these compounds at room temperature with formation of formic acid and nondistilling resinous reaction products.

An attempt to cause 3,3,3-trichloropropene to react with cyclohexene in accordance with scheme (b) at 180-200° was not successful: the original amount of cyclohexene was recovered unchanged from the reaction mixture. It was found also that 1,1,2-trichloro-1,3-butadiene is unable to react as a diene in the Diels-Alder reaction, evidently because of the considerable delocalization of the π-electron cloud of the trichlorovinyl group and the resulting destruction of the π-π conjugation of the double bonds. We did not succeed in preparing adducts of 1,1,2-trichloro-1,3-butadiene with maleic anhydride and with cyclohexene in spite of wide variations in the reaction conditions (100-180°, 2-8 hours, in benzene and without solvent). On the other hand, 1,1,2-trichloro-1,3-butadiene was found to be a very active dienophile; reaction occurs at the vinyl group and an adduct is formed with cyclopentadiene under relatively mild conditions (80°, benzene):
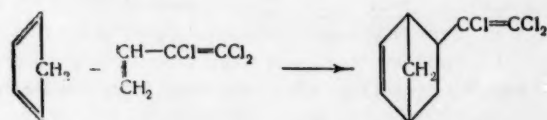
When the reaction is carried out in absence of solvent, 1,1,2-trichloro-1,3-butadiene vigorously polymerizes without giving the diene-synthesis product.

The presence of a trichlorovinyl group in the adduct formed by 1,1,2-trichloro-1,3-butadiene with cyclopentadiene was proved by its conversion by means of sodium into the corresponding substituted acetylene, which

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* It was earlier shown that the system $CCl_2=CH-$ does not combine with mercuric acetate [11].

was characterized as its Ag and Hg derivatives:
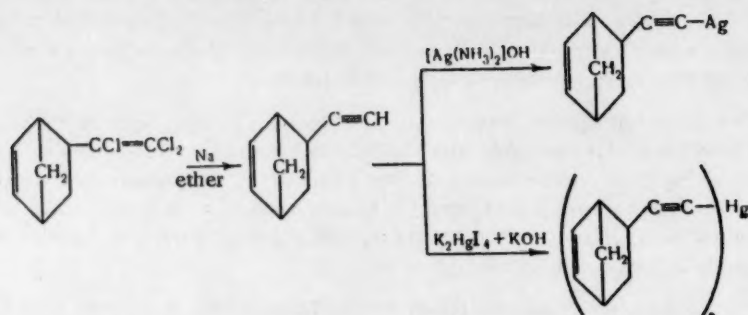
EXPERIMENTAL

5-(Trichloromethyl)bicyclo[2.2.1]hept-2-ene. A mixture of 54 g (0.37 mole) of 3,3,3-trichloropropene, 25 g (0.38 mole) of cyclopentadiene, 0.05 g of hydroquinone, and 30 ml of benzene was heated for six hours at 180-200° in sealed tubes. Two distillations through a column gave 45 g (57%) of 5-(trichloromethyl)bicyclo-[2.2.1]hept-2-ene; b. p. 93° (9 mm); $n^{20}D$ 1.5270; d^{20}_4 1.3280; found MR 48.97; for $C_8H_9Cl_3F$, calculated MR 48.87. Found: C 45.99; 46.00; H 4.23; 4.22%. $C_8H_9Cl_3$. Calculated: C 45.43; H 3.29%. The residue in the distillation flask was a viscous polymer.

Reaction of 5-(trichloromethyl)bicyclo[2.2.1]hept-2-ene with mercuric acetate. To a warm solution of 5.4 g (1.7 mmoles) of mercuric acetate in 30 ml of methanol, 3.6 g (1.7 mmoles) of 5-(trichloromethyl)-bicyclo[2.2.1]hept-2-ene was added. The mixture was left for 12 hours and then poured into a hot sodium chloride solution; after 30 minutes the liquid was decanted, and 5 ml of methanol was added to the residue; after 12 hours the precipitate of vic-(chloromercuri)methoxy-2-(trichloromethyl)norcamphane was filtered off and crystallized twice from acetone. Yield 2 g (42%); m. p. 140° (decomp.). Found: C 23.22; 23.48; H 2.40; 2.54; Cl 29.45; 29.64%. $C_9H_{12}Cl_4HgO$. Calculated: C 22.66; H 2.33; Cl 29.69%.

2-(Trichloromethyl)norcamphane. A mixture of 15 g (7.1 mmoles) of 5-(trichloromethyl)bicyclo[2.2.1]-hept-2-ene, 15 g of methanol, and 0.13 g of platinum black was prepared in a hydrogenation flask, which was mounted on a shaker. The reaction mixture was shaken in an atmosphere of hydrogen for 20 hours at about 20°, and the solution was then filtered off. The filtrate was distilled, and a fraction of b. p. 62.5-63° (3 mm) was collected; this was 2-(trichloromethyl)norcamphane together with a little 5-(trichloromethyl)bicyclo[2.2.1]-hept-2-ene. The fraction was purified from the latter by treatment with an excess of a solution of mercuric acetate in methanol. After 12 hours the mixture was poured into water and 2-(trichloromethyl)norcamphane was extracted with ether. The extract was dried over calcium chloride, and vacuum distillation then gave 9 g (59%) of pure 2-(trichloromethyl)norcamphane; b. p. 92° (9 mm); $n^{20}D$ 1.5170; d^{20}_4 1.3060. found MR 49.47; for $C_8H_{11}Cl_3$. calculated MR 49.35. Found: C 45.20; 45.24; H 5.01; 5.26%. $C_8H_{11}Cl_3$. Calculated: C 45.01; H 5.20%.

5-(Dichloromethylene)bicyclo[2.2.1]hept-2-ene. To a solution of 29 g (13.7 mmoles) of 5-(trichloro-methyl)bicyclo[2.2.1]hept-2-ene in 25 ml of 2-methoxyethanol at 70-80° a solution of an equimolecular amount of potassium hydroxide in 25 ml of 2-methoxyethanol was added dropwise with stirring. The mixture was heated further for one hour at 90-100° and then poured into water; the lower layer was separated, washed with water, and dried over calcium chloride. Two distillations gave 16 g (67%) of 5-(dichloromethylene)bicyclo[2.2.1]-hept-2-ene; b. p. 96° (25 mm); $n^{20}D$ 1.5350; d^{20}_4 1.2374; found MR 44.05; for $C_8H_7Cl_2 2F$, calculated MR 43.54. Found: C 54.33; 54.36; H 4.55; 4.52; Cl 40.62; 40.77%. $C_8H_7Cl_2$. Calculated: C 54.90; H 4.61; Cl 40.52%.

Reaction of 5-(dichloromethylene)bicyclo[2.2.1]hept-2-ene with mercuric acetate. A solution of 5.1 g (16 mmoles) of mercuric acetate in 30 ml of methanol was added to an emulsion of 1.4 g (8 mmoles) of 5-(dichloromethylene)bicyclo[2.2.1]hept-2-ene in 5 ml of methanol; the mixture was left at about 20° for 12 hours and then poured into a solution of 10 g of sodium chloride in 40 ml of water; after one hour the clear solution was decanted and treated with excess of 10% sodium hydroxide. The precipitated mercuric oxide was

filtered off, washed with alcohol and ether, and dried at 50°. The weight of HgO was 1.8 g, which corresponds to 8.3 mmoles of mercuric acetate that did not react. When the oily residue remaining after the decantation was ground with ether, crystals were obtained of vic-(chloromercuri)methoxy-2-(dichloromethylene)norcamphane, m. p. (after two crystallizations from 1:1 chloroform-ether) 154.5-156°; yield 0.5 g (14%). Found: C 24.42; 24.37; H 2.37; 2.56%. $C_9H_{11}Cl_3HgO$. Calculated: C 24.50; H 2.29%.

5-(Trichlorovinyl)bicyclo[2.2.1]hept-2-ene.

A mixture of 38 g (0.24 mole) of 1,1,2-trichloro-1,3-butadiene, 16 g (0.24 mole) of cyclopentadiene, and 0.05 g of hydroquinone in 30 ml of dry benzene was heated in sealed tube at 80° for six hours. Benzene was distilled off, and two vacuum distillations of the residue through a column gave 15 g (27%) of 5-(trichlorovinyl)bicyclo[2.2.1]hept-2-ene; b. p. 83-84° (3 mm); $n^{20}D$ 1.5468; d^{20}_4 1.3372, found MR 53.00; for $C_9H_9Cl_3 2F$, calculated MR 53.03. Found: C 48.46; 48.17; H 3.98; 3.93; Cl 47.60; 47.67%. $C_9H_9Cl_3$. Calculated: C 48.36; H 4.06; Cl 47.60%.

5-Ethynylbicyclo[2.2.1]hept-2-ene.

One-third of a solution of 20 g (0.09 mole) of 5-(trichlorovinyl)-bicyclo[2.2.1]hept-2-ene in 50 ml of ether was added to a stirred suspension of 8.2 g (0.36 g-atom) of finely divided sodium in 50 ml of ether. The mixture was warmed slightly, and after five minutes a vigorous reaction set in, and it was necessary to apply external cooling with ice water from time to time. The remainder of the ethereal solution of 5-(trichlorovinyl)bicyclo[2.2.1]hept-2-ene was added dropwise over a period of 60 minutes. After 12 hours 50 ml of methanol was added to the reaction mixture; when the mixture ceased to foam, it was poured into water, the layers were separated, the aqueous layer was extracted with ether, and the ether extract was added to the organic layer, which was dried over calcium chloride. Vacuum distillation through a column gave 7.3 g (69.5%) of 5-ethynylbicyclo[2.2.1]hept-2-ene, a mobile liquid with sharp odor; b. p. 54-55° (29 mm); $n^{20}D$ 1.4922; d^{20}_4 0.9227; found MR 37.17; for $C_9H_{10}FF$; calculated MR 36.89. Found: C 91.31; 91.39; H 8.47; 8.48%. C_9H_{10}. Calculated: C 91.45; H 8.55%.

Silver derivative of 5-ethynylbicyclo[2.2.1]hept-2-ene.

A 25% solution of ammonia was added dropwise to a solution of 0.17 g (1 mmole) of silver nitrate in 5 ml of distilled water until the precipitate formed redissolved, and a solution of 0.12 g (1 mmole) of 5-ethynylbicyclo[2.2.1]hept-2-ene in 5 ml of methanol was then added. The precipitate of the silver derivative of 5-ethynylbicyclo[2.2.1]hept-2-ene was filtered off, washed with alcohol and ether, and vacuum-dried. Yield 0.22 g (about 100%). The silver derivative chars in the range 130-140°, and when heated rapidly to 300° it decomposes with an explosion. Found: Ag 48.07; 48.33%. C_9H_9Ag. Calculated: Ag 47.93%.

Mercury derivative of 5-ethynylbicyclo[2.2.1]hept-2-ene.

A solution of 0.82 g (2.47 mmoles) of potassium iodide in 2 ml of water was added to a solution of 0.33 g (1.22 mmoles) of mercuric chloride in 3 ml of distilled water, and when the precipitated formed redissolved 1 ml of 10% potassium hydroxide solution was added. The very small precipitate was separated by centrifugation, and the clear solution was stirred while dropwise addition was made of 0.24 g (1 mmole) of 5-ethynylbicyclo[2.2.1]hept-2-ene in 10 ml of methanol. After 15 minutes the precipitate of the mercury derivative was filtered off, washed with 5 ml of ice-cold methanol, and crystallized from ethanol; yield 0.28 g (63.5%); m. p. 150.5-151.5°. Found: C 49.56; 49.63; H 4.14; 4.28; Hg 45.77; 45.65%. $C_{18}H_{18}Hg$. Calculated: C 49.71; H 4.17; Hg 46.12%.

SUMMARY

1. 3,3,3-Trichloropropene reacts with cyclopentadiene in accordance with the usual scheme of the diene synthesis.

2. In the Diels-Alder reaction 1,1,2-trichloro-1,3-butadiene reacts only as a dienophile.

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SYNTHESIS OF CYCLIC POLYORGANOSILOXANES CONTAINING VARIOUS GROUPS IN THE RING

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The synthesis of polyorganosiloxanes having linear molecular chains presents considerable difficulties. Usually, the hydrolysis of bifunctional monomers results in the formation of a mixture of products of low molecular weight having linear and cyclic structures; moreover, reaction proceeds mainly in the direction of cyclic products [1]. It is supposed that the cohydrolysis of bifunctional monomers also leads mainly to the formation of mixed cyclic compounds. In this connection the preparation of polyorganocyclosiloxanes and their subsequent conversion into linear polymers acquires great interest. In the literature there are reports of the preparation of polydimethylcyclosiloxanes [2], polydiethylcyclosiloxanes [3], polymethylphenylcyclosiloxanes, and some cyclic compounds containing a methyl or ethyl and hydrogen simultaneously attached to silicon [4].

Cyclic compounds containing both dimethylsiloxane and other units simultaneously have not been described in the literature. The development of methods for the preparation and transformation of mixed polyorganocyclosiloxanes is of great theoretical and practical interest because, on the one hand, it enables us to establish the effects of various groups on ring formation and the transformations of the products, and on the other, it enables us to obtain linear polymers containing various organic groups on the silicon atom arranged in a strictly defined order. No methods have yet been developed for the preparation of linear polymers in which there is a regular alternation of various groups along the polymer chain, and there is no information in the literature on this matter.

In the present investigation attempts were made to prepare polyorganocyclosiloxanes in which the ring contains dimethylsiloxane residues together with methylphenyl-, (chlorophenyl)methyl-, or diphenyl-siloxane residues in various relative amounts. The method of preparing mixed polyorganocyclosiloxanes was based on the cohydrolysis of two different bifunctional monomers with water in an acid medium.

$$n\,R_2SiCl_2 + m\,RR'SiCl_2 + (n + m)\,H_2O \rightarrow (PR'SiO)_m\,(R_2SiO)_m + 2\,(n + m)\,HCl$$
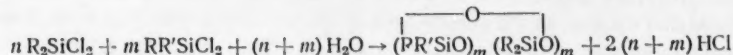
In accordance with this scheme we carried out the cohydrolysis of dichlorodimethylsilane with dichloromethylphenylsilane, with dichloro(chlorophenyl)methylsilane, and with dichlorodiphenylsilane. The experiments showed that in the cohydrolysis of the above bifunctional compounds with excess of water at ratios of dichlorodimethylsilane to the other component of 1 : 1 and 1 : 0.74, cyclic compounds containing mainly eight-membered rings were always obtained; also, the ratios of the amounts of the dimethylsilane and the other organosiloxane group in the ring were 1 : 1 and 3 : 1. In the isolation of individual polyorganocyclosiloxanes no six-membered rings were found. If such compounds are formed, then they are formed in extremely small amount and we did not succeed in isolating them by fractionation. However, under the conditions of hydrolysis described, compounds containing more units in the ring were always formed in considerable amount. Thus, in the cohydrolysis of dichlorodimethylsilane with dichloromethylphenylsilane, apart from eight-membered cycles we isolated

Compound	B.p. in °C (p in mm)	d_4^{20}	n_D^{20}	MR found	MR calc.	η at 20° (centistokes)	E (cal)
Octamethylcyclotetrasiloxane (CH₃)₂Si—O—Si—(CH₃)₂ / O O / (CH₃)₂Si—O—Si—(CH₃)₂	64(12)	0,9413	1,4013	74,5	74,47	3,3	—
Heptamethylphenylcyclotetrasiloxane (CH₃)₂Si—O—Si—(CH₃)₂ / O O / (CH₃)₂Si—O—Si(C₆H₅)(CH₃)	111—113 (7)	1,0163	1,4490	94,59	94,36	6,16	4827
Hexamethyldiphenylcyclotetrasiloxane (CH₃)₂Si—O—Si(C₆H₅)(CH₃) / O O / (CH₃)₂Si—O—Si(C₆H₅)(CH₃)	167—168 (7)	1,0602	1,4881	113,58	113,94	16,47	5730
Octamethyltetraphenylcyclohexasiloxane C₆H₅ CH₃ C₆H₅ / (CH₃)₂Si—O—Si—O—Si / O O CH₃ / (CH₃)₂Si—O—Si—O—Si(C₆H₅)(CH₃) / C₆H₅ CH₃	182 (2)	1,0916	1,5170	190,34	190,24	46,23	—
Hexamethyldiphenylcyclotetrasiloxane (CH₃)₂Si—O—Si(C₆H₅)₂ / O O / (CH₃)₂Si—O—Si(CH₃)₂	166—170 (8)	1,0623	1,4880	113,68	113,94	21,08	7709
(chlorophenyl)heptamethylcyclotetrasiloxane (CH₃)₂Si—O—Si(CH₃)₂ / O O / (CH₃)₂Si—O—Si(C₆H₄Cl)(CH₃)	150 (18)	1,0882	1,4557	97,88	98,50	10,49	5873
Bischlorophenylhexamethylcyclotetrasiloxane	182—184 (4)	1,1756	1,4989	121,99	122,56	41,88	10384

octamethyltetraphenylcyclohexasiloxane, i.e., a twelve-membered cycle. In other cases we have not yet succeeded in isolating higher cycles. In the cohydrolysis of dichloro(chlorophenyl)methylsilane with dichlorodimethylsilane we have succeeded in isolating only eight-membered cycles with relative amounts of dimethylsiloxane and (chlorophenyl)methylsiloxane residues of 1:1 and 3:1. In the cohydrolysis of dichlorodimethylsilane with dichlorodiphenylsilane we isolated only one eight-membered cycle in which the ratio of the amounts of dimethylsiloxane to diphenylsiloxane was 3:1. In all cases the eight-membered cycles were readily isolated in good yield.

All the polyorganocyclosiloxanes isolated are stable liquids which can be readily vacuum-distilled without decomposition. The structures of the compounds obtained were established from their elementary compositions, infrared spectra, and qualitative reactions for functional groups. A test with sodium for hydroxy groups was negative. The infrared spectra of heptamethylphenylcyclotetrasiloxane and hexamethyldiphenylcyclotetrasiloxane were found to contain frequencies characteristic for Si—C₆H₅ (1429 cm⁻¹), Si—CH₃ and Si—(CH₃)₂ (1259 and 800 cm⁻¹), and Si—O—Si in an eight-membered ring (1080-1090 cm⁻¹). The properties of the com-

pounds obtained are given in the table. The viscosities of the polyorganocyclosiloxanes synthesized were investigated at different temperatures, and it was shown that introduction of a (chlorophenyl)methyl-, phenyl-methyl-, or diphenyl-siloxane residue into the ring in place of a dimethylsiloxane residue leads to a sharp increase in viscosity. The effect of a pair of phenyl groups on the viscosity depends on whether the two groups are both on the same silicon atom or are on two different silicon atoms. The cycle containing two phenyl groups on one silicon atom has the higher viscosity (see table).

Calculation of the activation energy for viscous flow E over temperatures ranging from $-10°$ to $+50°$ for different cycles showed that E is greatly dependent on the number of phenyl groups in the ring (see table).

Preliminary experiments showed that the cyclic compounds are capable of being polymerized under the action of catalysts. Questions concerned with the mechanism and kinetics of the polymerization of such cycles will be the subject of a separate communication.

EXPERIMENTAL

Cohydrolysis of dichlorodimethylsilane with dichloromethylphenylsilane. A mixture of 42 g of dichloro-dimethylsilane (1 mole) and 46 g of dichloromethylphenylsilane (0.74 mole) was added over a period of one hour to a stirred mixture of 60 ml of water and 100 ml of ether. The temperature was kept at about 30°. Stirring was continued further for about one hour. The layer of hydrolysis product was separated, washed with water, and dried with anhydrous sodium sulfate. After repeated fractional distillation we isolated: a) octamethyl-cyclotetrasiloxane, b. p. 64° (12 mm); yield 5.05%. Found: C 32.69; 32.60; H 8.12; 8.30; Si 37.02; 36.97%. $C_8H_{24}Si_4O_4$. Calculated: C 32.43; H 8.10; Si 37.50%; b) heptamethylphenylcyclotetrasiloxane, b. p. 111-113° (7 mm); yield 11.7%. Found: C 42.90; 43.02; H 7.66; 7.54; Si 31.04; 30.96%. $C_{13}H_{26}Si_4O_4$. Calculated: C 43.57; H 7.26; Si 31.8%; c) hexamethyldiphenylcyclotetrasiloxane, b. p. 167-168° (7 mm); yield 21.8%. Found: C 50.68, H 7.04; 7.05; Si 26.85; 27.06%. $C_{18}H_{28}Si_4O_4$. Calculated: C 51.42; H 6.66; Si 26.66%; d) octamethyl-tetraphenylcyclohexasiloxane, b. p. 182° (2 mm); yield 18.1%. Found: C 55.20; 55.00; H 6.48; 6.59; Si 23.13; 23.0%. $C_{32}H_{44}Si_6O_6$. Calculated: C 55.49; H 6.35; Si 24.47%; e) high-boiling residue, yield 22.1%.

Cohydrolysis of dichlorodimethylsilane with dichlorodiphenylsilane. The method of cohydrolysis was analogous to that used in the preceding experiment. As a result of fractional distillation we obtained: a) hexa-methyldiphenylcyclotetrasiloxane, b. p. 166-170° (8 mm); yield 22.3%. Found: C 51.96; 52.20; H 7.16; 7.40; Si 25.59; 25.51%. $C_{18}H_{28}Si_4O_4$. Calculated: C 51.42; H 6.66; Si 26.66%; b) residue; yield 60.9%.

A similar procedure was used in the cohydrolysis of dichlorodimethylsilane with dichloro(chlorophenyl)-methylsilane. Fractional distillation gave: a) (chlorophenyl)heptamethylcyclotetrasiloxane, b. p. 150° (18 mm); yield 23.5%. Found: C 39.00; 38.97; H 6.10; 6.21; Si 27.92; Cl 9.30%. $C_{13}H_{25}Si_4O_4Cl$. Calculated: C 39.21; H 6.36; Si 28.53; Cl 9.04%; b) bischlorophenylhexamethylcyclotetrasiloxane, b. p. 182° (4 mm); yield 32.1%. Found: C 43.92; H 5.00; Si 22.32; Cl 14.03%. $C_{18}H_{26}Si_4O_4Cl_2$. Calculated: C 44.18; H 5.31; Si 22.96; Cl 14.51%.

SUMMARY

1. In the cohydrolysis of dichlorodimethylsilane with dichloromethylphenylsilane and with dichloro-diphenylsilane cyclic products are formed which contain both dimethylsiloxane and methylphenyl- or diphenyl-siloxane residues in the proportions of 3 : 1 and 1 : 1. In the cohydrolysis of dichlorodimethylsilane with dichloro-(chlorophenyl)methylsilane cyclic products are formed which contain both dimethylsiloxane and (chlorophenyl)-methylsiloxane residues in the proportions of 3 : 1 and 1 : 1.

2. The following new eight-membered cyclic compounds were synthesized: heptamethylphenylcyclo-tetrasiloxane, hexamethyldiphenylcyclotetrasiloxane, (chlorophenyl)heptamethylcyclotetrasiloxane, and bis-chlorophenylhexamethylcyclotetrasiloxane. A new twelve-membered cyclic compound was also synthesized: octamethyltetraphenylcyclohexasiloxane.

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DEHYDROHALOGENATION OF SOME ORGANOSILICON COMPOUNDS AND THE REARRANGEMENT OF TRICHLORO(1,2-DICHLORO-ALKYL)SILANES IN THEIR DEHYDROCHLORINATION WITH ALUMINUM CHLORIDE

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In previous papers [1-6] we reported various regularities observed in the dehydrochlorination of some organosilicon compounds. In particular, it was shown [1, 7] that quinoline eliminates the 2-chlorine from trichloro(1,2-dichloroethyl)silane, whereas aluminum chloride eliminates the 1-chlorine atom. Later [8, 9] it was found also that trichloro(1,2-dibromoethyl)silane behaves analogously in dehydrobromination with aluminum chloride:

$$Cl_3SiCHXCH_2X \quad \begin{matrix} \xrightarrow{\text{quinoline}} & Cl_3SiCX{=}CH_2 \\ \xrightarrow{AlCl_3} & Cl_3SiCH{=}CHX \end{matrix} \quad,$$
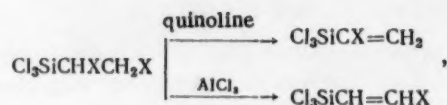
in which X = Cl or Br.

The results were unexpected, because we have shown conclusively [5, 6] that, irrespective of the dehydrochlorinating agent (quinoline or $AlCl_3$), the β-chlorine is always eliminated more readily than the α-chlorine.

In the dehydrochlorination of trichloro(1,2-dichloropropyl)silane, not only trichloro(1-chloropropenyl)-silane, but also a (chloroisopropenyl)silane, namely trichloro(2-chloro-1-methylvinyl)silane, was formed [3]:

$$Cl_3SiCHClCHClCH_3 \xrightarrow{AlCl_3} Cl_3SiCCl{=}CHCH_3 + Cl_3Si\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CHCl.$$
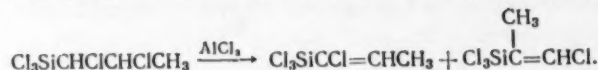
On the basis of the above facts, one of us [6] suggested a mechanism for the dehydrochlorination of trichloro(1,2-dichloroalkyl)silanes with aluminum chloride. This mechanism requires the elimination of the β-chlorine atom and isomerization of the β-carbonium ion formed with displacement of the Cl_3Si group from the α- to the β-carbon atom (see scheme 1):

$$\text{Scheme 1}$$

$$\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle X}{|}}{C}}l_3Si\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle Z}{|}}{C}}{-}H \xrightarrow{AlCl_3} \left[Cl_3Si\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle X}{|}}{C}}{-}\overset{+}{\underset{\underset{\displaystyle Z}{|}}{C}}H \rightleftarrows Cl\overset{+}{\underset{\underset{\displaystyle X}{|}}{C}}{-}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle Z}{|}}{C}}SiCl_3 \right] \rightarrow Cl_3Si\overset{\overset{\displaystyle Cl}{|}}{C}{=}CHZ + Cl_3Si\underset{\underset{\displaystyle X}{|}}{\overset{\overset{\displaystyle Cl}{|}}{C}}{=}\underset{Z}{C}Cl,$$
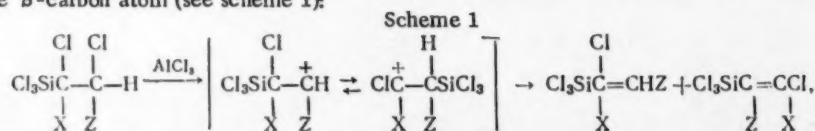
in which X and Z = H or CH_3.

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*L. A. Leites carried out the spectrographic part of the work.

The suggested scheme satisfactorily explains the structures of the products in the dehydrochlorination of trichloro (1,2-dichloroethyl)- and trichloro(1,2-dichloropropyl)-silanes. In fact, if X and Z are hydrogen atoms, then isomerization with migration of the Cl_3Si group goes completely, which gives the impression that the α-chlorine has been eliminated. If, however, X = H and Z = CH_3, isomerization with migration of the Cl_3Si group (admittedly partial) leads to the conversion of a propyl group into an isopropenyl group.

With the object of verifying this scheme, in the present investigation we subjected trichloro(1,2-dichloro-isopropyl)silane [trichloro(1,2-dichloro-1-methylethyl)silane] to dehydrochlorination with aluminum chloride; with quinoline this substance is dehydrochlorinated only to the chloroisopropenyl compound, trichloro(2-chloro-1-methylvinyl)silane [2]. After the dehydrochlorination of trichloro(1,2-dichloroisopropyl)silane with aluminum chloride we obtained an individual substance which did not correspond in its constants and in its Raman spectrum with either of the two possible [2] trichloro(chloroisopropenyl)silanes, $Cl_3SiC=CHCl$ and $Cl_3SiC-CHCl$. Thus,
$$\underset{CH_3}{|} \qquad \underset{CH_2}{\|}$$
the product could be one of six possible (chloropropenyl)- and (chloroallyl)-trichlorosilanes:

1) $Cl_3Si\overset{X}{\underset{|}{C}}=CH-CH_3$ 2) $Cl_3Si-CH=\overset{X}{\underset{|}{C}}-CH_3$ 3) $Cl_3SiCH=CH-CH_2X$

4) $Cl_3Si-\overset{X}{\underset{|}{CH}}-CH=CH_2$ 5) $Cl_3SiCH_2-\overset{X}{\underset{|}{C}}=CH_2$ 6) $Cl_3SiCH_2-CH=CHX$

Compounds (1) and (6) were prepared previously, and their properties (Raman spectrum, $n^{20}D$, d^{20}_4, and b. p.) did not coincide with those of the unknown compound. To prove the structure of the product we carried out the transformations shown below (scheme 2), which enable us to state that the structure of the product is undoubtedly that of trichloro(2-chloropropenyl)silane, i.e, compound (2).

Scheme 2

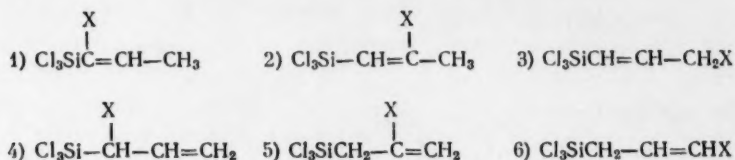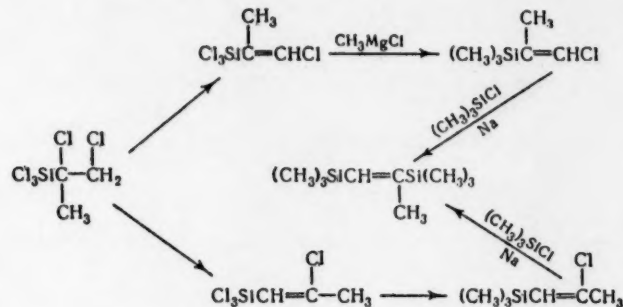The fact that the same product,$(CH_3)_3SiCH=CSi(CH_3)_3$, was obtained both by the upper route, with the
$$\underset{CH_3}{|}$$
aid of quinoline, and by the lower route, with the aid of $AlCl_3$, is reliably proved by the agreement between the Raman spectra and constants of these compounds. 1,2-Bistrimethylsilylpropene [3] was prepared again for this work by the upper route of scheme 2, and its properties were redetermined. As regards compounds (3), (4), and (5), in the transformations of scheme 2 they should form other bistrimethylsilylpropenes, some of which we have prepared previously [3].

Hence, the proposed mechanism of the dehydrochlorination of trichloro(1,2-dichloroalkyl)silanes becomes very probable. In fact, in the case of the dehydrochlorination of trichloro(1,2-dichloroisopropyl)silane scheme 1 (X = CH_3, Z = H) requires that the Cl_3Si group should migrate to the next carbon atom with conversion of an isopropyl group into a propenyl group, which is what actually happens. It is probable that the mechanism [1]

$$\overset{\displaystyle Cl}{\underset{\displaystyle |}{}}$$

of the dehydrochlorination of $Cl_3SiCHCH_2SiCl_3$, with aluminum chloride, which leads to the formation not only
of $Cl_3SiCH=CHSiCl_3$ but also of $Cl_3SiCSiCl_3$ (i.e., is also associated with migration of a Cl_3Si group), is of the

$$\overset{\displaystyle ||}{\underset{\displaystyle CH_2}{}}$$

same nature as that of the above-described rearrangement of trichloro(1,2-dichloroalkyl)silanes during their de-
hydrochlorination with aluminum chloride.

As regards the results of the dehydrochlorination of trichloro(2,3-dichloroalkyl)silanes with quinoline, we
have already stated [3] that two unsaturated compounds are formed in the dehydrochlorination of trichloro(2,3-
dichloropropyl)silane. In the present work we showed that in the dehydrochlorination of trichloro(2,3-dichloro-
isobutyl)silane two compounds are again obtained:

$$Cl_3SiCH_2\underset{\underset{CH_3}{||}}{C}-\overset{\overset{Cl}{|}}{\underset{\underset{}{}}{C}}\overset{Cl}{\underset{}{H_2}} \xrightarrow{\text{quinoline}} Cl_3SiCH_2-\underset{\underset{CH_2}{||}}{C}-CH_2Cl + Cl_3SiCH_2\underset{\underset{CH_3}{|}}{C}=CHCl$$
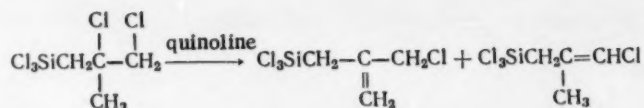
We may therefore conclude that in the dehydrochlorination of trichloro(1,2-dichloroalkyl)silanes with
quinoline only one unsaturated compound is formed and this has an α,β-double bond; on the other hand, in the
dehydrochlorination of trichloro(2,3-dichloroalkyl)silanes two unsaturated compounds are formed in which the
double bond has different positions.

It is known that chloro(3-chloroalkyl)silanes are not dehydrochlorinated at all with quinoline [4, 5]. When
these compounds do not contain a Cl_3Si group they cannot be dehydrochlorinated with aluminum chloride either
[1]. We therefore attempted to bring about the dehydrochlorination of $CH_3Cl\,2siCH_2CH_2CH_2Cl$ by pyrolysis at 600°
in an empty glass tube. It was found that allyldichloromethylsilane was formed in 48% yield. No admixture
of the expected dichloromethylpropenylsilane was detected, even in an analysis of the Raman spectrum.

$$CH_3Cl_2SiCH_2CH_2CH_2Cl \xrightarrow{600°} CH_3Cl_2SiCH_2CH=CH_2$$

Previously [4], in the pyrolysis of $Cl_2CH_3SiCH_2\underset{\underset{CH_3}{|}}{C}HCH_2Cl$ over activated charcoal we obtained somewhat

different results: it was shown that not only $CH_3Cl_2SiCH=C(CH_3)_2$ and $CH_3Cl_2SiCH_2-\underset{\underset{CH_3}{|}}{C}=CH_2$, but even

$Cl_2CH_3SiCH_2CH=CHCH_3$ was formed. This prompted us to repeat the pyrolysis of $CH_3Cl_2SiCH_2\underset{\underset{CH_3}{|}}{C}HCH_2Cl$ at 600°

in an empty glass tube in absence of activated charcoal. As a result of the pyrolysis we obtained a mixture of
two compounds, (2-methylallyl)- and (2-methylpropenyl)-dichloromethylsilanes (70: 30), but the formation of
2-butenyldichloromethylsilane was not observed.

The synthesis of the original dichloro(3-chloroalkyl)methylsilanes was generally carried out under pressure
in an autoclave at about 160° in presence of platinized charcoal as catalyst [4, 10]:

$$CH_2=CHCH_2Cl + HSiCl_2CH_3 \xrightarrow{\sim160°} ClCH_2CH_2CH_2SiCl_2CH_3$$
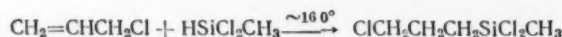
In the present investigation we found that this reaction is readily carried out in an ordinary flask in pres-
ence of chloroplatinic acid by boiling the mixture for 2-4 hours. Under these conditions we even succeeded in
bringing about the addition of dichloromethylsilane to allyl bromide, which does not occur under the autoclave

conditions. However, the addition of CH_3Cl_2SiH to 2-methylallyl chloride under these conditions went so violently that it was necessary to modify the procedure and to add the reaction mixture slowly to the catalyst in the flask. In these cases the yields of dichloro(3-chloroalkyl)methylsilanes were higher than those obtained by the old autoclave method [10]. Also, we showed that $Cl_3SiCH_2CH_2Br$ is readily dehydrobrominated with N,N-diethylaniline, whereas $Cl_3SiCH_2CH_2Cl$ is not dehydrochlorinated at all with this reagent.

The results enable us to assert that in organosilicon compounds bromine is much more mobile than chlorine in dehydrohalogenation. Incidently, the original (α- and β-bromoalkyl)trichlorosilanes were carried out for the first time by us by Speier's method [11], i.e., simultaneous passage of chlorine and bromine under visible irradiation. This method of preparing trichloro(haloalkyl)silanes is much more convenient and rapid than the chlorination of analogous compounds in ultraviolet radiation.

EXPERIMENTAL

Dichloro(3-chloropropyl)methylsilane $CH_3Cl_2SiCH_2CH_2CH_2Cl$. A mixture of 160 g of allyl chloride and 240 g of dichloromethylsilane was prepared in a 1 liter flask fitted with thermometer and reflux condenser. Addition was made to the mixture of 1 ml of a 0.1 N solution of $H_2PtCl_6 \cdot 6H_2O$ in isopropyl alcohol, and the contents of the flask were boiled until the temperature had risen to 75-80°, which generally required 3-4 hours. Further boiling did not lead to further rise in temperature. Distillation through a column gave 165 g of trichloromethylsilane, b. p. 65-66°, and 160 g (40%) of dichloro(3-chloropropyl)methylsilane, b. p. 184-185° and $n^{20}D$ 1.4600. The literature [10] gives: yield 30%; b. p. 184.5° (754 mm); $n^{20}D$ 1.4580.

When this reaction is carried out with the procedure of the next experiment, 2 kg of mixture can be treated in 3-4 hours without reduction in the yield of dichloro(3-chloropropyl)methylsilane.

Dichloro(3-chloroisobutyl)methylsilane $ClCH_2CHCH_2SiCH_3Cl_2$. A 15-20 ml portion of a mixture consist-
$$|$$
$$CH_3$$
ing of 209 g of 2-methylallyl chloride and 267 g of dichloromethylsilane was introduced into a 500 ml flask fitted with reflux condenser, thermometer, and dropping funnel. Speier's catalyst (1 ml) was added, and the mixture was heated; when it was certain that the reaction had started (the b. p. reached about 100°), the rest of the mixture was added at such a rate that the contents of the flask did not fall below 100°. Distillation through a column gave 60 g of trichloromethylsilane and 162 g (70%) of dichloro(3-chloroisobutyl)methylsilane, b. p. 195-196° (745 mm) and $n^{20}D$ 1.4630. The literature [10] gives: yield 58%; b. p. 195.5° (745 mm); $n^{20}D$ 1.4629.

(1-Bromoethyl)trichlorosilane $Cl_3SiCHBrCH_3$ and (2-bromoethyl)trichlorosilane $Cl_3SiCH_2CH_2Br$. Trichloroethylsilane (357 g) was introduced into a flask fitted with stirrer, reflux condenser, dropping funnel, and tube for the passage of chlorine. The contents of the flask were illuminated from below with a 200 w electric lamp and were stirred while chlorine was passed in a continuous stream of bubbles. The addition of 175 g of bromine was carried out at such a rate that the contents of the flask were always colored with bromine. When the whole of the bromine had been added and the liquid became colorless, the contents were fractionated through a column. We obtained 43 g of unchanged trichloroethylsilane, 49 g of (1-bromoethyl)trichlorosilane [b. p. 155.2° (747 mm); $n^{20}D$ 1.4802; d^{20}_4 1.6287; found MR 42.31; calculated MR 41.48], and 73 g of (2-bromoethyl)trichlorosilane [b. p. 171° (747 mm); $n^{20}D$ 1.4901; d^{20}_4 1.6990; found MR 42.01; calculated MR 41.48]. The residue consisted of 162 g of polybromoethyltrichlorosilanes.

Raman spectrum of $Cl_3SiCH_2CH_2Br$

($\Delta \nu$, cm^{-1}): 170 (4 b), 229 (1 b), 260 (1), 280 (3), 430 (1), 457 (10 b), 548 (1 b), 583 (2 b), 641 (10 b), 691 (0 b), 755 (2), 1021 (1), 1166 (1), 1262 (5), 1382 (0), 1439 (1), 2870 (1), 2900 (3), 2934 (1), 2961 (3).

Bromination of $Cl_3SiCH(CH_3)_2$. Trichloroisopropylsilane (300 g) [5] was brominated for 3.5 hours with 135 g of bromine with illumination and passage of chlorine under the conditions described for the preceding experiment. Fractionation through a column gave 45 g of unchanged $Cl_3SiCH(CH_3)_2$, b. p. 117-118°, and 230 g of a mixture of (1- and 2-bromoisopropyl)trichlorosilanes, b. p. 165-170° and m. p. 85-100°. The yield was 62% on the $Cl_3SiCH(CH_3)_2$ that reacted. In addition, 62 g of higher-boiling (170°) liquid polybromo compounds was obtained.

Dehydrobromination of $Cl_3SiCH_2CH_2Br$. A mixture of 104 g of (2-bromoethyl)trichlorosilane and 76 g of N,N-diethylaniline was slowly distilled from a 200 ml flask until the boiling point reached 180°. Redistillation of the condensate through a column gave 27 g (50%) of trichlorovinylsilane, b. p. 92°.

Dehydrobromination of $BrC_3H_6SiCl_3$. A mixture of 230 g of (1- and 2-bromoisopropyl)trichlorosilanes and 146 g of N,N-diethylaniline was slowly distilled from a Wurtz flask until the boiling point reached 200°. In distillation of the condensate through a column we collected only 10 g from 50° to 100°, but we obtained 120 g (77%) of trichloroisopropenylsilane, b. p. 112° (745 mm) and $n^{20}D$ 1.4455. The literature [2] gives b. p. 113.5°, (731 mm) and $n^{20}D$ 1.4453.

Trichloro[2-(chloromethyl)allyl]silane $Cl_3SiCH_2C{-}CH_2Cl$ and trichloro(2,3-dichloroisobutyl)silane

$$\overset{\textstyle CH_2}{\overset{\textstyle \|}{}}$$
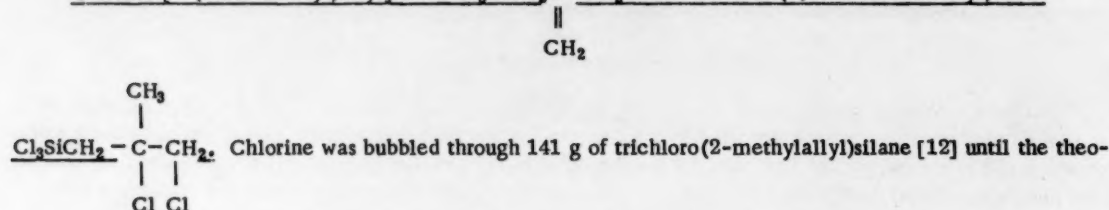
$Cl_3SiCH_2-\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle Cl\ \ Cl}{|\ \ \ \ |}}{C}}-CH_2.$ Chlorine was bubbled through 141 g of trichloro(2-methylallyl)silane [12] until the theo-

retical increase in weight was attained, which required ten hours. Distillation through a column gave two fractions: 1) 50 g of b. p. 180-200°, and 2) 68 g of b. p. 210-220°. Further distillation was accompanied by much decomposition. Refractionation of the first fraction gave 40 g of trichloro[2-(chloromethyl)allyl]silane; b. p. 187-188°; $n^{20}D$ 1.4850; d^{20}_4 1.3480. The literature [13] gives: b. p. 188-189°; $n^{20}D$ 1.4846; d^{20}_4 1.3473. Methylation of this product with methylmagnesium chloride gave a 65% yield of [2-(chloromethyl)allyl]trimethylsilane; b. p. 160.6° (748 mm); $n^{20}D$ 1.4513; d^{20}_4 0.9000. The literature [13] gives: b. p. 162-163° (768 mm); $n^{20}D$ 1.4510; d^{20}_4 0.8996.

Redistillation of the second fraction gave 50 g of trichloro(2,3-dichloroisobutyl)silane; b. p. 211-212°; $n^{20}D$ 1.5072. Found: Si 10.60; 10.30%. $C_4H_7SiCl_5$. Calculated: Si 10.78%.

Dehydrochlorination of $Cl_3SiCH_2-\overset{\overset{\textstyle Cl}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}-CH_2Cl.$ A mixture of 150 g of trichloro(2,3-dichloroisobutyl)-

silane and 74.4 g of quinoline was distilled from a 200 ml flask until the boiling point reached about 200°. Redistillation of the condensate through a column gave 27 g (20%) of a substance of b. p. 176-180°. The product was methylated with methylmagnesium chloride prepared from 9 g of magnesium in 300 ml of ether. The reaction mixture was boiled for four hours, and after the usual treatment distillation through a column gave 7.5 g (67%) of a substance of b. p. 157-162°.
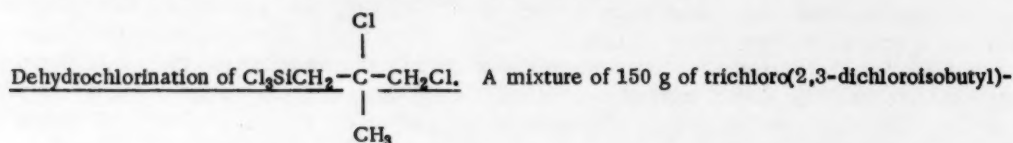
Raman spectrum KPC

($\Delta\nu$, cm^{-1}): 148 (1), 185 (1 b), 237 (2 b), 294 (1), 410 (0 b), 488 (1), 596 (10), 615 (5), 699 (3 b), 753 (2 b), 848 (1 b), 1024 (1 b), 1102 (1 b), 1130 (1 b), 1154 (2 b), 1182 (2), 1207 (0 b), 1256 (2 b), 1299 (2 b), 1323 (1), 1380 (1), 1415 (2 b), 1448 (1 b), 1630 (10), 1647 (10), 2892 (10), 2955 (10), 3007 (0), 3077 (2 b).

In the region of the spectrum containing frequencies of $C{=}C$ valence vibrations there are two lines of equal intensity, 1630 and 1647 cm^{-1}; the substance is therefore a mixture of two compounds that are present in approximately equal amounts. Some of the lines of the spectrum belong to $(CH_3)_3Si-\overset{\underset{\textstyle |}{}}{CH_2}-C{=}CH_2$ [13].

$$\underset{\textstyle CH_2Cl}{\underset{\textstyle |}{}}$$

There are no lines corresponding to $(CH_3)_3SiCH{=}C-CH_2Cl$. The other component of the mixture is probably

$$\underset{\textstyle CH_3}{\underset{\textstyle |}{}}$$

$(CH_3)_3SiCH_2-C=CHCl.$
$\quad\quad\quad\quad\quad\quad |$
$\quad\quad\quad\quad\quad CH_3$

$\quad\quad\quad\quad\quad\quad\quad\quad Cl$
$\quad\quad\quad\quad\quad\quad\quad\quad |$
<u>Dehydrochlorination of $Cl_3SiC-CH_2Cl$</u>.   A mixture of 120 g of trichloro(1,2-dichloroisopropyl)silane and
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad |$
$\quad\quad\quad\quad\quad\quad\quad\quad\quad CH_3$
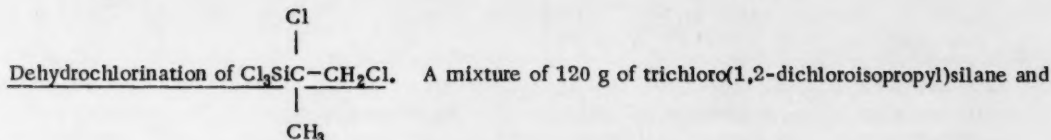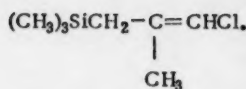
1 g of aluminum chloride was vacuum-distilled (about 150 mm). Redistillation of the condensate through a column gave 211 g (40%) of trichloro(2-chloro-1-methylvinyl)silane, b. p. 155-157°; b. p. 155.5°(744 mm); $n^{20}D$ 1.4795; d^{20}_4 1.3812; found MR 43.14; calculated MR 42.80. F o u n d: Cl 67.52; 67.57%. $C_3H_4SiCl_4$ Calculated: Cl 67.54%.

Raman spectrum of KPC $Cl_3Si-CH=CCl-CH_3$

($\Delta\nu$, cm^{-1}): 151 (1), 172 (3), 193 (6), 247 (1 b), 298 (2), 322 (5), 358 (2), 395 (3), 438 (3), 463 (0), 493 (10), 508 (1), 591 (2 v. b)700 (2), 811 (0), 981 (2), 1040 (0), 1279 (0), 1388 (2), 1438 (3), 1616 (10), 2876 (1 b), 2931 (5 b), 2970 (1), 3017 (1).

$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad Cl$
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad |\,^{\centerdot}$
<u>(2-Chloropropenyl)trimethylsilane $(CH_3)_3SiCH=C-CH_3$</u>. To CH_3MgCl prepared from 16 g of magnesium
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad Cl$
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad |$
in 300 ml of ether we added 31 g of $Cl_3SiCH=C-CH_3$. The contents of the flask were boiled for three hours, and were then decomposed with water. The ether layer and the ether extracts from the aqueous layer were dried

$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad C$
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad |$
with calcium chloride. Fractionation through a column gave 13 g (60%) of $(CH_3)_3SiCH=C-CH_3$; b. p. 130-132°; $n^{20}D$ 1.4413; d^{20}_4 0.8875; found MR 44.30; calculated MR 43.91.
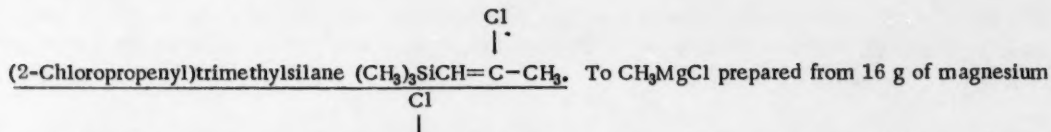
Raman spectrum KPC

($\Delta\nu$, cm^{-1}): 151 (1), 184 (2 b), 230 (3v. b), 304 (1), 341 (0), 397 (1), 443 (3 sh), 478 (2), 497 (1), 582 (8), 629 (8), 703 (3 b), 848 (b), 1017 (1), 1225 (1 b), 1323 (0), 1381 (2), 1415 (1), 1444 (3 b), 1622 (8 b), 2843 (0), 2899 (10 b), 2919 (2 b), 2960 (10 b).

The structure ascribed to this compound is confirmed by its Raman spectrum. In fact, the absence of frequencies higher than 3000 cm^{-1} characterizing the $=CH_2$ group indicates that compounds (4) and (5) need not be considered. The presence of the frequency 1380 cm^{-1} is characteristic of the 2-methylpropenyl group, and the structure $(CH_3)_3SiCH=C-CH_3$ is similar to that of trimethyl(2-methylpropenyl)silane.
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad |$
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad Cl$

<u>1,2-Bistrimethylsilylpropene $(CH_3)_3SiCH=CSi(CH_3)_3$</u>.   Sodium (6 g) was granulated very finely in 30 ml
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad |$
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad CH_3$
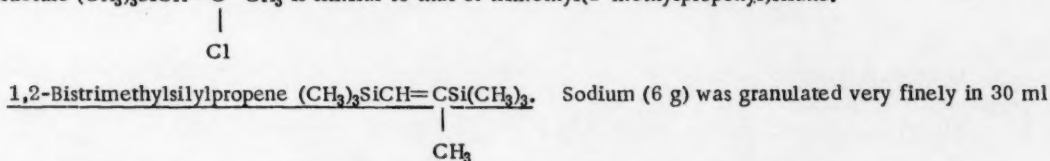
of boiling toluene by means of a rapidly rotating stirrer. The suspension was cooled, and the toluene was poured off and replaced by 200 ml of ether. Addition was made of 13.2 g of $(CH_3)_3SiCl$, 1 ml of ethyl acetate, and a little $(CH_3)_3SiCH=CClCH_3$; when the reaction started the remaining 18 g of $(CH_3)_3SiCH=C-CH_3$ was added
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad |$
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad Cl$

in such a way that the ether boiled gently. The contents of the flask were boiled for ten hours and then filtered off from salt, which was washed with fresh ether. Distillation through a column gave 8 g (40%) of 1,2-bistrimethylsilylpropene, b. p. 162°.

($\Delta \nu$, cm^{-1}): 150 (3 b), 183 (3 b), 223 (2 v.b.) 315 (1 v.b) 373 (1), 426 (0.6), 465 (0.5), 504 (3), 588 (0), 619 (10), 645 (3), 696 (4 b), 848 (1 b), 962 (0), 1253 (2 b), 1291 (1 b), 1314 (1 b), 1368 (1 b), 1411 (2 b), 1444 (1 b), 1564 (4 b), 2845 (0 b), 2897 (10 b), 2957 (10 b).

With the exception of the lines at 504 and 645 cm^{-1}, the spectrum completely coincides with that of $(CH_3)_3SiCH=CSi(CH_3)_3$ synthesized in a different way [2, 3]. The lines at 504 and 645 cm^{-1} probably indicate
$$\qquad\qquad\qquad | \\ \qquad\qquad\qquad CH_3$$
the presence of $[(CH_3)_3Si]_2C=CH-CH_3$.

<u>Dehydrochlorination of $CH_3Cl_2SiCH_2CH_2CH_2Cl$.</u> Dichloro(3-chloropropyl)methylsilane (222 g) was passed over a period of five hours (one drop every two seconds) through an empty glass tube (diameter 16 mm, length 100 mm) at 600°. Distillation of the condensate through a column gave 16 ml of material coming over between 80° and 113°, 43 g (48%) of allyldichloromethylsilane, b. p. 119-120°, and 117 g of unchanged $CH_3Cl_2Si(CH_2)_3Cl$.

Raman spectrum KPC

($\Delta \nu$, cm^{-1}): 150 (2), 167 (1 b), 230 (3 b), 296 (1 b), 413 (4 b), 469 (10), 549 (2 b), 610 (1 b), 706 (3 b), 805 (2 b), 917 (1 b), 988 (0), 1109 (0 b), 1171 (4 b), 1247 (0), 1302 (6 sh), 1390 (3), 1422 (3), 1635 (10), 2907 (8 b), 2975 (4 b), 3008 (3 b), 3085 (2).

The spectrum confirms the structure $CH_3Cl_2SiCH_2-CH=CH_2$ since the lines at 413, 917, 988, 1302, 1390, 1635, and 3085 cm^{-1} are characteristic of an allyl group attached to a silicon atom [14].

<u>Dehydrochlorination of $CH_3Cl_2SiCH_2CHCH_2Cl$.</u> The pyrolysis of 270 g of dichloro(3-chloroisobutyl)methyl-
$$\qquad\qquad\qquad\qquad\qquad\qquad | \\ \qquad\qquad\qquad\qquad\qquad\qquad CH_3$$
silane was carried out for four hours under the conditions of the preceding experiment. Distillation of the condensate through a column gave 29 g of material boiling between 70° and 130° and 54 g (28%) of a substance of b. p. 140-149°; 105 g of the original dichloro(3-chloroisobutyl)methylsilane was recovered unchanged. Methylation of 54 g of the fraction of b. p. 140-149° with methylmagnesium chloride (from 20 g of magnesium in 500 ml of ether) was carried out in the usual way. Fractionation through a column gave 23 g (56%) of a fraction of b. p. 108-110°. Analysis [4, 15] of the Raman spectrum of this compound indicated that only $(CH_3)_3SiCH_2C=CH_2$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad | \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad CH_3$$
(about 70%) and $(CH_3)_3SiCH=C-CH_3$ (about 30%) were present.
$$\qquad\qquad\qquad\qquad | \\ \qquad\qquad\qquad\qquad CH_3$$

SUMMARY

1. In the dehydrochlorination of trichloro(1,2-dichloroisopropyl)silane with aluminum chloride, trichloro-(2-chloropropenyl)silane is formed. This isomerization is a special case of a general rearrangement undergone by all trichloro(1,2-dichloroalkyl)silanes when dehydrochlorinated with aluminum chloride.

2. A mechanism is proposed for this new arrangement in the organic chemistry of silicon; it consists in partial or complete migration of a trichlorosilyl group from the 1- to the 2-carbon atom after the elimination of the 2-chlorine atom, which leads to the formation of trichloro(2-chloro-1-alkenyl)silanes.

3. Whereas the dehydrochlorination of a trichloro(1,2-dichloroalkyl)silane gives only one unsaturated compound, the same reaction with a trichloro(2,3-dichloroalkyl)silane gives a mixture of two different unsaturated organosilicon compounds.

4. A method was developed for the synthesis of dichloro(3-chloroalkyl)methylsilanes under mild conditions without use of an autoclave, and it was shown that unsaturated compounds can be synthesized in good yield by the pyrolysis of these compounds.

5. In dehydrohalogenation, a bromine atom in an alkyl chain of an organosilicon compound is much more readily eliminated than an analogous chlorine atom.

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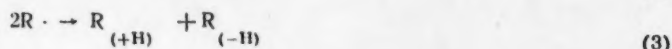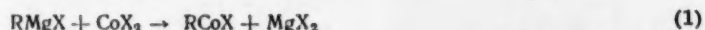*Original Russian pagination. See C. B. Translation.

REACTIONS OF ORGANOMETALLIC COMPOUNDS WITH HEAVY-METAL SALTS

COMMUNICATION 1. REACTION OF ETHYLMAGNESIUM BROMIDE WITH TITANIUM AND COBALT HALIDES

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Several investigations have been devoted to the reactions between organomagnesium compounds and various metal salts. Kondyrev and Fomina [1], who investigated this reaction for the first time, showed that the reaction of alkylmagnesium halides with heavy-metal salts (iron, copper, cobalt, chromium, molybdenum, and other salts) led to equivalent amounts of saturated and unsaturated hydrocarbons corresponding to the alkyl of the organomagnesium compound. The heavy-metal salts are then reduced to salts of the metals in lower valence states, or in some cases to the metal. Investigations on the mechanism of these reactions have been recently reported in the literature, in particular those of Gilman [2, 3], Kharash [4], Ziegler [5], and Herman [6]. These authors suppose that the reaction of alkylmagnesium halides with heavy-metal salts passes through the stage of unstable organometallic compounds, whose decomposition is usually regarded as a free-radical process:

$$RMgX + CoX_2 \rightarrow RCoX + MgX_2 \tag{1}$$

$$RCoX \rightarrow R\cdot + \cdot CoX \tag{2}$$

$$2R\cdot \rightarrow R_{(+H)} + R_{(-H)} \tag{3}$$

Other investigators, e.g., Wilds [7] consider that the decomposition of the organometallic compounds leads to the direct formation of hydrocarbons without participation of free radicals; this, however, was not proved experimentally.

It is doubtful whether free radicals are formed in this reaction. It is known [8] that free ethyl radicals preferentially react with the solvent with abstraction of an H atom and formation of ethane. Disproportionation is here found only to a slight extent. On the other hand it is found in most of the investigations cited that the decomposition of ethylmagnesium bromide under the action of heavy-metal salts is associated with the formation of equivalent or comparable amounts of ethane and ethylene.

With the object of determining the mechanism of the reaction, we studied the reaction of ethylmagnesium bromide with titanium tri- and tetra-chlorides in presence of nitric oxide, of styrene, and of α-methylstyrene. All these compounds trap free radicals quantitatively, so that the study of their effect on the yields of ethane and ethylene can lead directly to the establishment of the occurrence of free-radical stages. If the view that C_2H_5 radicals appear during the reaction is correct, the presence of acceptors should completely prevent the formation of ethane and ethylene. We showed that the presence of nitric oxide, styrene, or α-methylstyrene during the reaction of ethylmagnesium bromide with titanium tetrachloride at 20° has no effect on the total yield or relative amounts of ethane and ethylene (Table 1).

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Reaction of Ethylmagnesium Bromide with Titanium Tetrachloride at 20° (Duration of expt. 2 hours)

Molar ratio $\frac{C_2H_5MgBr}{TiCl_4}$	Yield (%) of			Acceptor	
	ethane	ethylene	ethane and ethylene	name	amount (% on vol. of reaction mixture)
1 : 1,6	52	20	72	No acceptor	—
1 : 1,6	56	18	74	" "	—
1 : 1,6	56	20	76	Nitric oxide	—
1 : 1,6	54	21	75	" "	—
1 1,6	57	23	80	α-Methylstyrene	50
1 : 1,6	57	18	75	"	50
1 : 1,6	57	21	78	Styrene	55
1 : 1,6	56	23	79	"	60

TABLE 2

Reaction of Ethylmagnesium Bromide with Titanium Trichloride at 100°C (Duration of expt. 5 hours)

Molar ratio $\frac{C_2H_5MgBr}{TiCl_3}$	Yield (%) of			Acceptor
	ethane	ethylene	ethane and ethylene	
1 : 2,4	31	11	42	No acceptor
1 : 2,4	34	13	47	"
1 : 2,4	32	12	46	Nitric oxide
1 : 2,4	30	14	44	"
1 : 2,4	39	15	54*	α-Methylstyrene
1 : 2,4	40	15	55*	"

* In the last two experiments (Table 2) a more highly dispersed form of titanium trichloride was used.

TABLE 3

Reaction of Ethylmagnesium Bromide with Cobalt Chloride

Time of expt. (°C)	Time of expt. (hours)	Molar ratio $\frac{C_2H_5MgBr}{CoCl_2}$	Yield (%) of			Acceptor	
			ethane	ethylene	ethane and ethylene	name	amount (% on vol. or reaction mixture)
40	5	1 : 4,8	13	11	24	No acceptor	—
40	5	1 : 4,8	12	12	24	α-Methylstyrene	20
40	5	1 : 4,8	15	15	30	Styrene	20
20	5	1 : 4,8	15	12	27	No acceptor	—
20	5	1 : 4,8	17	15	32	Nitric oxide	—
20	5	1 : 4,8	15	14	29	Styrene	20
−20	7	1 : 4,8	15	12	27	No acceptor	—
−20	7	1 : 4,8	18	16	34	α-Methylstyrene	90
−20	7	1 : 4,8	18	15	33	Styrene	50

It must be pointed out that nitric oxide may react with organomagnesium compounds with formation of derivatives of nitrosohydroxylamine [9], which limits the possibility of its use for the quantitative trapping of free radicals. The fact that free-radical stages are absent in the reaction of ethylmagnesium bromide with titanium tetrachloride becomes obvious when styrene and α-methylstyrene are used as acceptors of free radicals.
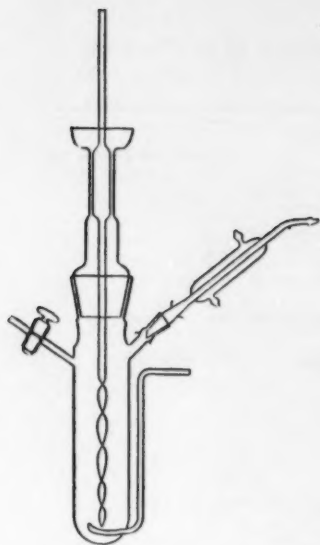
Fig. 1. Reactor.

These compounds were taken in large excess to avoid the possibility of their being consumed completely by polymerization under the action of TiCl$_4$ (or the complex formed in the reaction between C$_2$H$_5$MgBr and TiCl$_4$). We showed by bromide-bromate titration that there remained 15-20% of unused styrene or α-methylstyrene in the reaction mixture at the end of the experiment.

Similar results were obtained in the study of the reaction of ethylmagnesium bromide with titanium trichloride. In this case the experiments were carried out at 100° (Table 2).

The reaction between ethylmagnesium bromide and cobalt chloride was studied in presence of the same free-radical acceptors. The results that we obtained at temperatures ranging from −20° to +40° show that none of the acceptors brings about a reduction in the yield of ethane and ethylene (Table 3).

It is noteworthy that, particularly in the case of TiCl$_3$ and CoCl$_2$, the total yield of ethane and ethylene differs substantially from the theoretical yield. This is associated with the fact that unchanged organomagnesium compound remains in the system. We showed that the total yield of hydrocarbons becomes almost quantitative (97-99%) if the reaction mixture is decomposed with water after the completion of the reaction between ethylmagnesium bromide and cobalt chloride.

The data presented in Tables 1-3 enable us to conclude that, at least over the temperature ranges studied, free-radical stages are absent in the reaction between ethylmagnesium bromide and titanium or cobalt salts. It should be noted that in presence of titanium tri- or tetra-chloride the yield of ethane is substantially higher than that of ethylene. A similar observation was made by Gilman [3], who showed that, in the reaction of ethylmagnesium bromide with titanium tetrachloride at 25° (at a ratio of 4:1) in diethyl ether, the yields of ethane and ethylene were 52% and 9%, respectively. The author explains this fact by reaction of C$_2$H$_5$· radicals with the solvent. We do not regard this conclusion as well founded, for in presence of free ethyl radicals styrene and α-methylstyrene should almost completely suppress the formation of ethane and ethylene. Our results show that the presence of these acceptors affects neither the over-all yield of ethane and ethylene nor the relative amounts of these. It is probable that the formation of ethylene in an amount smaller than that of ethane is associated with the partial polymerization of ethylene under the action of the complex formed in the reaction between titanium salts and ethylmagnesium bromide. It was recently shown that complexes of this type may be used for the polymerization of olefins [10]. On the other hand, in the reaction between cobalt chloride and ethylmagnesium bromide, which has not been caused to bring about the initiation of polymerization, ethane and ethylene are formed in equivalent amounts.

The amount of polyethylene that can be formed under the conditions under which we carried out reaction between titanium halides and ethylmagnesium bromide is extremely small. For this reason we were unable to prove the formation of polymer experimentally.

EXPERIMENTAL

To eliminate the possibility of the introduction of the vapor of low-boiling solvent into the gaseous reaction products, ethylmagnesium bromide was synthesized in a medium of diisopentyl ether (b. p. 171°). The resulting solution was diluted with eight times the amount of dry kerosene (150-220° fraction). The same fraction was used as solvent in all other cases. The concentration of organomagnesium compound was determined from the amount of hydrocarbons obtained by decomposition of a definite volume of its solution with water. The dehydration of cobalt chloride hexahydrate was effected by prolonged heating at 150-170° in a vacuum (2 mm) or in a stream of dry hydrogen chloride at 250°, in accordance with the procedure described in the literature [11, 12]. Commercial titanium tetrachloride was purified by distillation through a column having a filling of copper turnings. Titanium trichloride was prepared by the reduction of titanium tetrachloride with hydrogen at

800°. The product was freed from traces of titanium tetrachloride by heating it in a vacuum (2 mm) at 170° for eight hours. Nitric oxide, which was prepared by Karyakin's method [11], was carefully dried over KOH and P_2O_5.

The experiments were carried out in a 100 ml apparatus fitted with stirrer, condenser, and tap for the introduction of the necessary solutions (Fig. 1). Before an experiment the apparatus was repeatedly evacuated and filled with dry nitrogen. Cobalt chloride and titanium trichloride were introduced into the apparatus in a countercurrent of nitrogen. The ethylmagnesium bromide solution was introduced from a Schlenk apparatus under a pressure of nitrogen. Titanium tetrachloride, styrene, and α-methylstyrene were introduced in the same way.

When nitric oxide was used as acceptor, it was bubbled through the reaction mixture throughout the experiment.

The gaseous products of the reaction were collected in a gas buret. At the end of the reaction dry carbon dioxide was bubbled through the reaction mixture at the same temperature to carbonate the unchanged ethylmagnesium bromide. The amount of carbon dioxide necessary for complete carbonation was established by blank experiments, which were carried out at 40°, 20°, and −20°. For the complete removal of the gaseous products dissolved in the kerosene, the temperature was raised to 100° and a large volume of nitrogen was blown through the mixture.* The amount of nitrogen required for the complete liberation of ethane and ethylene dissolved in the reaction mixture was also established by blank experiments. The ethane and ethylene contents of the gas were determined with the aid of a VTI gas-analyzer. We describe typical experiments below.

Reaction of ethylmagnesium bromide with titanium tetrachloride. For reaction we took 20 ml of ethylmagnesium bromide solution (0.41 mole/liter) and 30 ml of a kerosene solution of $TiCl_4$ (0.53 mole/liter). The experiment was carried out for two hours at 20° with vigorous stirring. Dry carbon dioxide was then bubbled through the reaction mixture at the same temperature. The temperature was raised to 100°, and the apparatus was purged with nitrogen. The total volume of gas was 1068 ml at STP. Contents of hydrocarbons in gas: ethane 9.2% (52% yield), ethylene 3.5% (20% yield).

Reaction of ethylmagnesium bromide with titanium tetrachloride in presence of styrene. For reaction we took 20 ml of ethylmagnesium bromide solution (0.61 mole/liter), 26 ml of styrene, and 23.5 ml of a kerosene solution of $TiCl_4$ (0.39 mole/liter). The experiment ran for two hours at 20°. The treatment was as for the preceding experiment. The total volume of gas was 1113 ml at STP. Contents of hydrocarbons in gas: ethane 6.8% (57% yield), ethylene 2.5% (21% yield). The unconsumed styrene in the reaction mixture, determined by titration by the bromide-bromate method, amounted to 17% on the amount taken.

Reaction of ethylmagnesium bromide with cobalt chloride. For reaction we took 5.73 g of anhydrous cobalt chloride and 50 ml of ethylmagnesium bromide solution (0.16 mole/liter). The experiment was for five hours at 20°. The treatment was as in the first experiment. The total volume of gas was 1050 ml at STP. Contents of hydrocarbons in gas: ethane 2.5% (15% yield), ethylene 2.0% (12% yield).

SUMMARY

1. A study was made of the reaction of ethylmagnesium bromide with titanium tri-and tetra-chlorides and with cobalt chloride in presence of various free-radical acceptors.

2. The presence of free-radical acceptors affects neither the yield of ethane and ethylene nor their relative amounts, which indicates that there are no free-radical stages in the given reaction.

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INVESTIGATION OF THE RELATIVE REACTIVITIES OF MULTIPLE
BONDS IN THE ORGANOMETALLIC COMPOUNDS OF GROUP IV
BY THE THIOCYANOGEN-VALUE METHOD

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Some years ago we discovered [1, 2] that some organosilicon compounds containing unsaturated groups do not give the theoretical bromine values (BV) when these are determined by Kaufman's method [3]. Thus, all organosilicon compounds containing the allyl or 2-methylallyl group gave higher than the calculated value of BV. For example, for trialkylallylsilanes ($R_3SiCH_2CH = CH_2$) the BV was found to be just double the theoretical value, but for di-, tri-, and tetra-allylsilanes no well-defined regularities were observed in the bromine values, and the results were rarely reproducible.

In explanation of this phenomenon we suggested [1, 2] that the thermally unstable compounds formed, which contain 2,3-dibromopropyl groups, undergo so-called β-decomposition (β-elimination):

$$R_3SiCH_2CH=CH_2 + Br_2 \rightarrow R_3SiCH_2CHBrCH_2Br \xrightarrow{t^\circ} R_3SiBr + CH_2=CHCH_2Br.$$
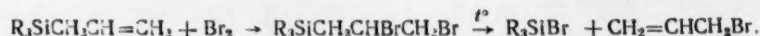
The allyl bromide eliminated combines with two bromine atoms (Kaufman's solution is usually taken in excess), which results in a doubling of the BV. In the case of polyallylsilanes, after the elimination of one or two groups the molecule becomes thermally stable and the remaining 2,3-dibromopropyl groups are not eliminated, or are eliminated very slowly. The magnitude of the BV therefore becomes indefinite and dependent on external conditions (temperature, time, etc.). Sila-hydrocarbons containing vinyl or 3-butenyl groups give the theoretical bromine values because the $R_3SiCHBrCH_2Br$ or $R_3SiCH_2CH_2CHBrCH_2Br$ formed, unlike $R_3SiCH_2CHBrCH_2Br$, is a thermally stable compound. Another group of organosilicon compounds that does not give the correct bromine values are those containing silicon-attached hydrogen, which reacts with the bromine of Kaufman's solution. Thus diallylsilane and allylsilane give high bromine values with Kaufman's solution because the bromine is partially consumed in the replacement of hydrogen in the Si—H bond.

Therefore, for the characterization of the purity of an unsaturated organosilicon compound we decided to use the addition of thiocyanogen at the multiple bond, or Kaufman's method of thiocyanogen values (TV) [4]. It was found the TV agrees closely with the calculated value for all classes of unsaturated organosilicon compounds. Thus, it became clear that thiocyanogen does not react with the Si—H bond and that the 2,3-dithiocyanatoalkylsilanes formed are thermally stable compounds, i.e., that the occurrence of thiocyanato groups (—SCN) on the β- and γ-carbon atoms (relative to the silicon atom) does not result in thermal β-elimination of allyl thiocyanate.

The apparent disadvantage of the TV method, as compared with the BV method, is the long time required in the determination of the TV of some unsaturated sila-hydrocarbons. Thus $(C_2H_5)_3SiCH = CH_2$ and some other 1-alkenylsilanes add thiocyanogen to saturation only after 24 hours. However, the slowness with which thiocyanogen adds made it possible for us to determine with ease the percentage of thiocyanogen added after various
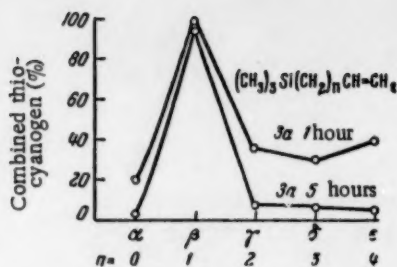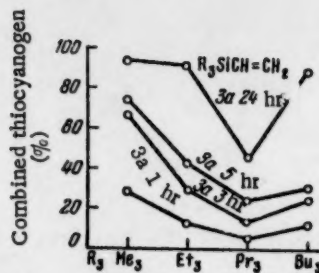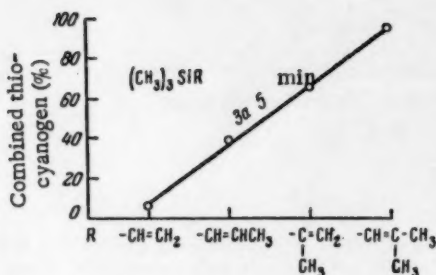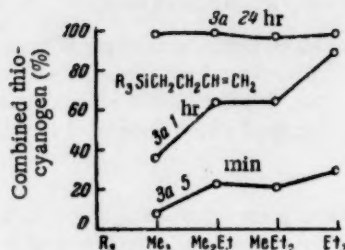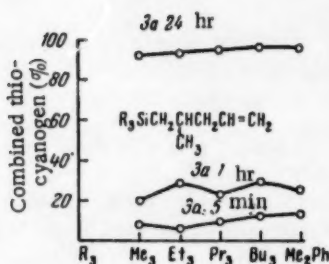
Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

intervals of time, i.e., to follow the rate of addition to a given unsaturated compound. Thus the TV method provided us with a simple tool for the determination of the relative reactivities of multiple bonds in various organosilicon compounds. Thus, the determination [5] of thiocyanogen values for the homologous series $R_3Si(CH_2)_nCH=CH_2$ enables us to establish an interesting correlation between the reactivity of the double bond and its position relative to the silicon atom (Fig. 1).

It is clear from Fig. 1 that the vinylsilanes (n = 0) are the least reactive and the allylsilanes (n = 1) are the most reactive. The same graph shows that 3-butenyl-silanes (n = 2) are considerably more reactive than vinyl-silanes (n = 0), but are less reactive than allylsilanes, etc. Finally, the results clearly indicate an alternation in the reactivity of the multiple bond: compounds for which n = 0 and 2 are of low reactivity, and compounds for which n = 1 have high reactivity.

This correlation was later confirmed several times in an examination of the same homologous series in other ionic addition reactions with HX, X_2, $(RO)_2PS_2H$, and other reagents. On the other hand, in free-radical addition reactions with compounds of this homologous series the reverse reactivity relation was found [6, 7], i.e., the compounds of the homologous series $R_3Si(CH_2)_nCH=CH_2$ which were the most reactive in ionic addition reactions (e. g., allylsilanes) were of low reactivity in free-radical addition reactions, and vice versa. On the basis of this fact we may regard the addition of thiocyanogen as an ionic addition reaction at the multiple bond.

By means of TV determinations we found the relation of the reactivity of the double bond in 1-alkenyl-silanes to the number and positions of the methyl groups bringing about the branching at the double bond (Fig. 2). For trialkylvinylsilanes ($R_3SiCH=CH_2$) the relation of the reactivity of the double bond to the nature of R is shown in Fig. 3. For the 3-alkenylsilane series the reactivity increases as we pass from methyl to ethyl groups
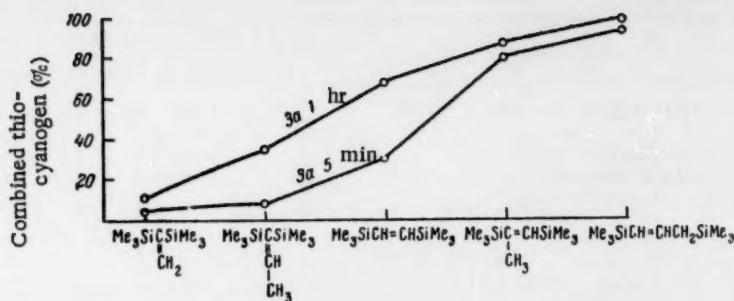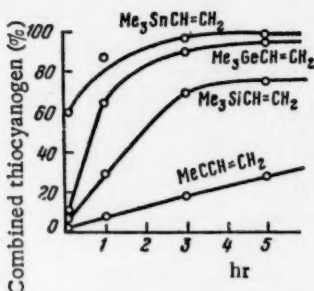
Fig. 6.

Fig. 7.

(Fig. 4). Finally, for 4-alkenylsilanes no correlation between the reactivity of the double bond and the structures of the other three groups could be found, for they all combined with thiocyanogen to almost the same extent, irrespective of the time (5 minutes, 1 hour, and 24 hours) (Fig. 5).

An interesting relation between reactivity and structure is observed for disilyl-ethylenes and -propenes (Fig. 6). We obtained particularly clear results in TV determinations on the compounds $(CH_3)_3MCH = CH_2$, in which M was varied in the following order: C, Si, Ge, Sn (Fig. 7). For compounds of the series $(CH_3)_3MCH_2CH = CH_2$ no similar relation could be established because for M = Si, Ge, and Sn about 100% addition of thiocyanogen occurred in only five minutes, i.e., so rapidly that differences in rates of addition could not be observed.

We thus established that the TV method is fully applicable also to unsaturated germanium and tin compounds. The scope of the TV method is somewhat restricted by the fact that the preparation of thiocyanogen and its addition reaction are carried out in glacial acetic acid. Acetic acid reacts with the groups SiCl, SiBr, SiOCH$_3$, etc. We therefore investigated only sila-, germa-, and stanna-hydrocarbons. We have thus proposed a very simple method, requiring only 0.1 g of substance, for the determination of the relative reactivities of a multiple bond in ionic addition reactions for various unsaturated organometallic compounds. The thiocyanogen values of various compounds, determined after various intervals of time, are given in the table.

EXPERIMENTAL

Method of determining thiocyanogen values [8, 9]. A 0.1 N solution of free thiocyanogen was prepared by the action of 0.6 ml of bromine on 6-7 g of lead thiocyanate in 200 ml of anhydrous acetic acid; the precipitate of PbBr$_2$ was then filtered off through a dried, double, fluted filter paper [4]. A weighed amount (about 0.1 g) of the substance to be tested was placed in a dry flask fitted with a ground stopper. By means of an automatic pipet, 20 ml of 0.1 N thiocyanogen in anhydrous acetic acid was added, and the reaction flask was placed in the dark. After a definite interval of time (5 minutes, 1 hour, etc.) 10 ml of potassium iodide solution was introduced into the flask, and the liberated iodine was titrated with 0.1 N thiosulfate. A parallel control experiment was carried out. The proportion of thiocyanogen added (degree of thiocyanogenation) was calculated as percent of the theoretical value from the formula:

$$A = \frac{(a - b)\,Mb}{200c},$$

in which A is the proportion of thiocyanogen that had reacted (%); a is the volume of 0.1 N thiosulfate required in the control experiment (ml); b is the volume of 0.1 N thiosulfate required in the experiment with the sample (ml); c is the weight of substance tested.

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TABLE

Formula	Thiocyanogenation (%)				
	5 min	1 hour	3 hours	5 hours	1 day
$(CH_3)_3SiCH=CH_2$	4,0	29,5	67,4	73,9	95,5
$(C_2H_5)_3SiCH=CH_2$	3,0	13,8	29,8	42,3	93,5
$(C_3H_7)_3SiCH=CH_2$	—	5,6	14,7	24,1	46,6
$(C_4H_9)_3SiCH=CH_2$	—	12,5	24,6	28,6	89,9
$(CH_3)_2Si(CH=CH_2)_2$	6,1	—	17,2	29,7	—
$Si(CH=CH_2)_4$	1,5	12,7	—	—	—
$(CH_3)_3SiC=CH_2$ CH_3	64,3	80,7	—	—	98,7
$C_3H_7(CH_3)_2SiCH=CHC_6H_5$ CH_3	29,5	40	53,4	—	—
$(CH_3)_3SiCH=C-CH_3$	98,3	101,4	—	—	—
$(CH_3)_3SiCH=CH-CH_3$	42,1	99,0	—	—	—
$(C_2H_5)_3S.CH=C-CH_3$ CH_3	74,9	96,5	—	—	—
$C_4H_9(CH_3)_2SiCH=C-CH_3$ CH_3	78,0	88,1	88,2	88,6	96,4
$(C_2H_5)_3SiCH=CH-CH_3$	35,8	87,3	—	—	99,0
$(CH_3)_3Si\langle\bigcirc\rangle$	5,8	18	34,6	41,5	85,6
$(CH_3)_3SiC-CH_2-CH_3$ CH_3	41,2	52,5	—	—	91,5
$(CH_3)_3SiC=CHCH_2OH$ CH_3	59,7	76,2	—	—	—
$(CH_3)_3SiCC_6H_5$ CH_2	4,1	10,6	19,6	24,3	71
$(CH_3)_2Si(CH=C-CH_3)_2$ CH_3	57,8	83,2	—	—	99,1
$(C_2H_5)_3SiCCl=CH_2$	0	0	—	—	3,0
$(CH_3)_3C-CH=CH_2$	3,6	8,4	18,6	26,8	57,2
$(C_2H_5)_3SnCH=CH_2$	58,2	80,9	86,7	88,9	96,2
$(CH_3)_4GeCH=CH_2$	20,8	65,9	88,3	94,2	94,2
$(CH_3)_3SnCH=CH_2$	60	83,2	94,3	98,7	—
$(CH_3)_3SiCH_2-CH=CH_2$	93,3	93,9	—	—	—
$(C_2H_5)_3SiCH_2-CH=CH_2$	96,4	96,4	—	—	—
$(C_3H_7)_3S.CH_2-CH=CH_2$	92,2	97,3	—	—	100,2
$(CH_3)_3SnCH_2-CH=CH_2$	78,9	94,2	—	—	—
$(C_2H_5)_3SnCH_2CH=CH_2$	76,4	—	101,2	103,8	104,0
$(CH_3)_3GeCH_2CH=CH_2$	96,0	102,0	—	—	—
$CH_3SiH(CH_2-CH=CH_2)_2$	76,8	93,7	—	—	—
$CH_3Si(CH_2-CH=CH_2)_3$	81,6	95,6	—	—	—
$(C_2H_5)_2Si(CH_2-CH=CH_2)_2$	83,7	88,5	—	—	90,8
$(CH_3)_2Si(CH_2-CH=CH_2)_2$	94,8	96,9	—	—	109,1
$CH_3(C_3H_7)Si(CH_2-CH=CH_2)_2$	87,0	91,9	—	—	95,3
$(C_4H_9)_2Si(CH_2-CH=CH_2)_2$	55,9	90,3	—	—	98,3
$(C_6H_5)(CH_3)Si(CH_2-CH=CH_2)_2$	72,9	91,4	—	—	93,8
$(C_3H_7)HSi(CH_2CH=CH_2)_2$	87,1	113,8	—	—	103,1
$C_3H_7Si(CH_2CH=CH_2)_3$	69,6	83,8	—	—	91,3
$C_6H_5Si(CH_2-CH=CH_2)_3$	64,4	80,7	—	—	91,2
$(CH_3)_2Si(CH_2C=CH_2)_2$ CH_3	54,2	65,5	—	—	73,6
$(C_2H_5)_3SiCH_2C=CH_2$ CH_3	97,2	99,3	—	—	—
$(CH_3)_3SiCH_2C=CH_2$ CH_3	93,3	96,8	—	—	104,8
$(CH_3)_3GeCH_2C=CH_2$ CH_3	103,4	—	—	—	—
$(CH_3)_2SiCH=CH-CH=CH-CH_3$ CH_3	100,5	102,4	—	—	—
$(CH_3)_3SiCH_2CH=CCl-CH_3$	0	0	—	1,0	10,4

TABLE (continued)

Formula	Thiocyanogenation (%) in				
	5 min	1 hour	3 hours	5 hours	1 day
$(CH_3)_3SiCH_2CH_2CH=CH_2$	6,9	37,7	—	—	99,6
$(C_2H_5)(CH_3)_2SiCH_2CH_2CH=CH_2$	22,5	61,8	—	—	102,4
$(C_2H_5)_2CH_3SiCH_2CH_2CH=CH_2$	20,1	60,3	—	—	100,6
$(C_2H_5)_3SiCH_2CH_2CH=CH_2$	30,4	90,3	—	—	102
$(CH_3)_3SiCH_2CH_2C=CH_2$ $\quad\quad CH_3$	96,3	97,7	—	—	102,6
$(CH_3)_3SiCH-CH_2CH=CH_2$ $\quad\quad CH_3$	8,5	20,3	—	—	93,9
$(C_2H_5)_3SiCH_2CHCH_2CH=CH_2$ $\quad\quad\quad CH_3$	5,2	31,2	—	—	93,0
$(C_2H_5)_3SiCH_2C-CH_2-CH_2-CH=CH_2$ $\quad\quad\quad CH_3$	9,3	16,9	—	—	90,1
$(C_3H_7)_3SiCH_2CH-CH_2CH=CH_2$ $\quad\quad\quad CH_3$	10,2	22,0	—	—	95,6
$(C_4H_9)_3SiCH_2CHCH_2CH=CH_2$ $\quad\quad\quad CH_3$	12,7	29,4	—	—	98,6
$(CH_3)_2(C_6H_5)SiCH_2CHCH_2CH=CH_2$ $\quad\quad\quad CH_3$	13,8	24,1	—	—	96,2
$(CH_3)HSi(CH_2CHCH_2CH=CH_2)_2$ $\quad\quad\quad CH_3$	5,2	39,1	—	—	98,4
$(CH_3)_3Si(CH_2)_4CH=CH_2$	3,2	40,2	—	—	97,7

Thiocyanogenation of disilyl derivatives

Formula	5 min	1 hour	3 hours	5 hours	1 day
$(CH_3)_3SiCH=CHSi(CH_3)_3$	29,8	67,5	—	—	90,6
$(C_2H_5)_3SiCH=CHSi(C_2H_5)_3$	5,6	9,9	—	—	59,?
$(CH_3)_3SiCH=CSi(CH_3)_3$ $\quad\quad\quad CH_3$	90,0	97,4	98,4	99	101,5
$(C_2H_5)_3SiOCH_2CH=CSi(C_2H_5)_3$ $\quad\quad\quad\quad CH_3$	7,8	27,5	—	—	68,2
$(CH_3)_3SiC\cdot Si(CH_3)_3$ $\quad\quad HCCH_2$	34,6	46,6	68,8	75,6	--
$(CH_3)_3SiCH_2CH=CHSi(CH_3)_3$	96	98	100	—	—
$(CH_3)_3SiCSi(CH_3)_3$ $\quad\quad CH_2$	4,3	8,8			61,4

SUMMARY

1. The determination of the thiocyanogen values of unsaturated compounds of Si, Ge, and Sn provides a more general method for the estimation of unsaturation than the bromine-value method.

2. The determination of thiocyanogen values can serve as a convenient and rapid method for the determination of the relative reactivities of unsaturated organometallic compounds in ionic reactions of addition at a multiple bond.

3. In the homologous series $R_3Si(CH_2)_nCH=CH_2$ the variation in the reactivity of the double bond can be expressed as $\beta > \gamma > \alpha$, and for the compounds $R_3MCH=CH_2$ (M = C, Si, Ge, or Sn) it can be expressed as $C < Si < Ge < Sn$.

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DEHYDROGENATION OF HYDROCARBONS OVER ALUMINA-CHROMIA CATALYSTS CONTAINING ADDITIONS OF CERTAIN METAL OXIDES

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In our preceding investigation [1] we showed that additions of K_2O, introduced as KOH, K_2CO_3, KNO_3, or $K_2Cr_2O_7$, to alumina-chromia catalysts substantially change their stabilities and activities in the dehydrogenation of isopentane, hexane, and cyclohexane. It was found also that these additions reduce the yields of unsaturated hydrocarbons from hexane.

In the present investigation we decided to investigate the same reactions in presence of an alumina-chromia catalyst with additions of Li_2O, Na_2O, Rb_2O, and Cs_2O and to compare the results with the existing data on the alumina-chromia catalyst. It was of interest also to investigate the dehydrogenation of isopentane, hexane, and cyclohexane in presence of an alumina-chromia catalyst having additions of ZnO or PbO. By the use of these catalysts we hoped to suppress aromatization in the dehydrogenation of hexane and in this way to increase the olefin: benzene ratio in the products obtained from this hydrocarbon.

The investigation showed that the catalysts with additions of rubidium and cesium oxides are close in properties to an alumina-chromia-potassia catalyst. The best of the catalysts investigated for the dehydrogenation of hexane were alumina-chromia-lithia and alumina-chromia-litharge catalysts.

EXPERIMENTAL

All the catalysts investigated were prepared by the impregnation of active alumina with solutions of ammonium dichromate and lithium, rubidium, cesium, zinc, or lead nitrate. The procedure used in the preparation of such catalysts is described in our previous paper [1] for the case of the alumina-chromia-potassia catalysts. The relative amounts of the components were the same in all the catalysts: Al_2O_3 90.7 moles percent; Cr_2O_3 5.6 moles percent; additive 3.7 moles percent. The experimental procedure was the same as in the investigation cited above; also, the catalyzates were analyzed in the same way. The hydrocarbon (100 ml) was passed over the catalyst (30 ml) at 500° at a space velocity of 0.5 hour^{-1}. The results are presented in Table 1. Table 2 gives the yields of unsaturated and aromatic hydrocarbons (on the amount of the original hydrocarbon passed and on the amount that reacted) and the specific surfaces of the catalysts. Figure 1 represents the relation of catalyst activity in the dehydrogenation of isopentane, hexane, and cyclohexane and the dehydrocyclization of hexane to the time for which the catalysts operate within the limits of a 7-hour experiment.

It will be seen from the results that additions of sodium, potassium, rubidium, and cesium oxides to an alumina-chromia catalyst give catalysts of almost identical activities for the dehydrogenation of isopentane; in their presence isopentane gives 36-39% of unsaturated hydrocarbons (on the amount of original hydrocarbon passed). In the dehydrogenation of hexane over alumina-chromia catalyst with the above-indicated additions 9-12% of unsaturated hydrocarbons is obtained (on the amount of hexane passed). However, in presence of an

TABLE 1

Compositions of Liquid Catalyzates and Gases

Addition to alumina-chromia catalyst	Hydro-carbon	Yield of cata-lyzate	Content (%) in catalyzate of unsat-urated hydro-carbons [*]	aromatic hydro-carbons	n_D^{20}	Amount of gas (liters at STP)	Composition of gas H_2	C_nH_{2n}	C_nH_{2n+2}
Li₂O	Isopentane	89,/	33,4(0,9)	—	1,3641	10,750	83,6	2,1	14,3
	Hexane	86,1	19,3	17,2	1,3955	17,447	90,3	1,6	8,1
	Cyclohexane	81,6	Traces	77,6	1,4792	52,290	98,6	0,0	1,4
Na₂O	Isopentane	92,6	37,7(1,7)	—	1,3665	10,110	85,0	0,4	14,6
	Hexane	86,6	13,8	26,0	1,4040	21,760	92,4	0,0	7,6
	Cyclohexane	81,8	Traces	79,6	1,4810	50,600	95,9	0,0	4,1
K₂O	Isopentane	91,2	39,3(2,5)	—	1,3668	12,840	92,2	0,8	7,0
	Hexane	83,1	10,9	46,0	1,4315	37,090	93,2	2,3	4,5
	Cyclohexane	81,4	Traces	88,2	1,4890	55,900	99,0	0,4	0,6
Rb₂O	Isopentane	90,6	39,6(1,7)	—	1,3655	10,440	92,6	0,0	7,4
	Hexane	82,8	11,6	42,0	1,4210	33,834	96,8	0,0	3,2
	Cyclohexane	80,2	Traces	73,6	1,4755	46,563	95,8	0,0	4,2
Cs₂O	Isopentane	92,2	38,2(1,0)	—	1,3655	10,528	91,8	1,0	7,2
	Hexane	84,1	13,4	39,0	1,4190	30,900	95,2	0,9	3,9
	Cyclohexane	85,0	3,6	48,4	1,4555	30,700	97,8	0,4	1,8
ZnO	Isopentane	83,8	30,9(2,5)	—	1,3652	11,564	70,0	7,0	23,0
	Hexane	70,1	16,4	31,2	1,4102	30,803	61,7	15,8	22,5
	Cyclohexane	88,0	2,1	56,0	1,4610	36,500	99,2	0,8	0,0
PbO	Isopentane	86,1	31,4(2,0)	—	1,3630	10,080	91,8	1,3	6,9
	Hexane	87,8	17,8	15,2	1,3955	19,490	91,6	2,6	5,8
	Cyclohexane	91,1	Traces	33,0	1,4450	21,969	92,0	3,0	5,0

[*] The contents of unsaturated hydrocarbons in hexane and cyclohexane catalyzates are calculated for the corresponding monoolefins without taking account of the possible formation of dienes; for the isopentane catalyzate the contents of isopentenes and isoprene (in parentheses) are given separately.

TABLE 2

Yields of Dehydrogenation and Dehydrocyclization Products (% by weight on the amount of hydrocarbon passed and on the amount decomposed)

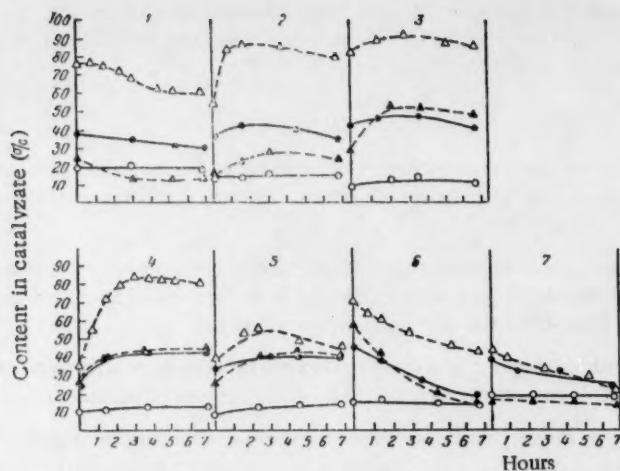| Addition to alumina-chromia catalyst	Specific surface (sq. m/g)	Unsaturated hydrocarbons, regarded as monoolefins — from isopentane in amt passed	on amt de-comp.	from hexane in amt passed	on amt de-comp.	Benzene from hexane in amt passed	on amt de-comp.	from cyclohexane in amt. passed	on amt. de-comp.	Ratio of yields of unsaturated and aromatic hydro-carbons on hexane passed
Li₂O	158	30,9	74,5	16,6	35,0	14,8	31,3	63,3	77,5	1,12
Na₂O	134	36,8	83,5	12,0	25,1	22,5	47,0	65,1	78,2	0,53
K₂O	144	38,6	81,4	9,1	14,2	38,2	59,5	77,8	80,7	0,24
Rb₂O	147	37,7	80,0	9,6	15,6	34,8	56,5	59,0	75,0	0,28
Cs₂O	154	36,3	82,4	11,3	18,8	32,8	54,7	41,1	73,1	0,35
ZnO	149	28,0	63,4	11,5	18,2	21,9	34,6	49,7	80,6	0,53
PbO	133	29,1	67,7	15,6	40,4	13,3	32,4	30,0	78,0	1,17

Fig. 1. Relation of contents of unsaturated (●−●− from iso-
pentane and O−O− from hexane) and aromatic (▲−−−▲−−−
from hexane and △−−−△−−− from cyclohexane) hydrocarbons
to the time for which alumina-chromia catalysts containing addi-
tions of metal oxides are in use: 1) Li_2O; 2) Na_2O; 3) K_2O; 4)
Rb_2O; 5) Cs_2O; 6) ZnO; 7) PbO.

alumina-chromia-natria catalyst hexane gives a much smaller amount of aromatic hydrocarbons (23% of hexane passed) than in presence of alumina-chromia with additions of potassium, rubidium, and cesium oxides (35-38%). In the dehydrogenation of cyclohexane all the catalysts investigated varied in activity in a way not related to the variation found in other reactions.

Alumina-chromia-lithia, alumina-chromia-litharge, and alumina-chromia-zinc oxide catalysts have lower activities in the dehydrogenation of isopentane and dehydrocyclization of hexane than alumina-chromia catalysts with additions of potassium, rubidium, and cesium oxides. However, the yields of unsaturated hydro-carbons obtained from hexane in presence of catalysts containing additions of lithium and lead oxides are higher (16-17%) than in presence of the other catalysts investigated (9-12%). As shown in our previous investigation [1], over an alumina-chromia catalyst without additions of metal oxides this yield is still larger, namely 20% on the amount of hexane passed. The specific surfaces of the catalyst varied in the range 134-158 sq.m/g and probably formed a determining factor in the reactions investigated.

From the experimental material obtained it may be concluded that catalysts having a high aromatizing power are active also in the dehydrogenation of isopentane. However, not all catalysts that are active in the dehydrogenation of isopentane have high aromatizing power. Hence, variation in the additions made to an alumina-chromia catalyst affects the extent to which dehydrogenation of isopentane occurs, but has less effect on the dehydrocyclization of hexane and the dehydrogenation of cyclohexane. It is probable that the aromatiza-tion of hexane requires some changes in the nature of the catalyst which are not essential for the dehydrogenation of isopentane.

As will be seen from the last column of Table 2, by the introduction of various additions in an alumina-chromia catalyst the relative yields of unsaturated and aromatic hydrocarbons obtained from hexane can be changed substantially, from 0.24 to 1.17. The highest ratios were obtained over catalysts with additions of lith-ium and lead oxides (1.12 and 1.17, respectively). The higher values of the ratios for these catalysts are asso-ciated with their relatively low activities in the aromatization reaction. Curves 1, 6, and 7 in Fig. 1, which were obtained with catalysts containing additions of lithium, zinc, and lead oxides and having lower aromatiz-ing powers, differ from the other curves. In the course of time the activities of these catalysts in the dehydro-genation of cyclohexane and isopentane and the dehydrocyclization of hexane fall appreciably, whereas the activities of the other catalysts either rise or pass through a maximum. It is noteworthy that in all cases the curve for the dehydrogenation of hexane is almost parallel to the axis of abscissae and the variation of the rate

of this reaction is not related to change in the rate of the aromatization of hexane. We came to the same conclusion in our study of the dehydrogenation of isopentane, hexane, and cyclohexane in presence of alumina-chromia-potassia catalysts prepared in different ways [1].

SUMMARY

1. A study was made of the dehydrogenation of isopentane, hexane, and cyclohexane in presence of an alumina-chromia catalyst containing additions of lithium, sodium, potassium, rubidium, cesium, zinc, and lead oxides at 500° at a space velocity of 0.5 hour^{-1}.

2. Catalysts containing sodium, potassium, rubidium, and cesium oxides are almost identical in activity in the dehydrogenation of isopentane and hexane; the yields of unsaturated hydrocarbons were 36-39% from isopentane and 9-12% from hexane (on the amount of hydrocarbon passed).

3. The catalysts with the highest dehydrocyclizing power were those with additions of potassium, rubidium, and cesium oxides; the yields of benzene were 35-38% on the amount of hexane passed.

4. Of all the catalysts investigated, the alumina-chromia-lithia and the alumina-chromia-litharge catalysts were the best from the point of view of high yields of unsaturated hydrocarbons (16-17% on the hydrocarbon passed) and low yields of benzene (13-15%).

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*Original Russian pagination. See C. B. Translation.

CATALYTIC TRANSFORMATIONS OF ISOPENTYLCYCLOPENTANE
IN PRESENCE OF HYDROGEN UNDER PRESSURE

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In the study of the catalytic transformations of alkylcyclopentanes (methyl- and ethyl-cyclopentanes) it was shown that at high temperatures (450-510°) and high pressures of hydrogen (20-50 atm) over Pt-Al$_2$O$_3$ [1], Ni-Al$_2$O$_3$ [2, 3], and Pb-, Rh-, and Ru-Al$_2$O$_3$ [4-6] they are isomerized with ring enlargement and formation of the corresponding cyclohexanes, which are subsequently dehydrogenated to aromatic hydrocarbons; rise in temperature was found to favor the formation of aromatic hydrocarbons. Under these conditions part of the alkyl-cyclopentanes underwent hydrogenolysis with formation of alkanes. The isomerization of cyclopentanes usually proceeds readily over bifunctional catalysts [7]. The use of dehydrogenating catalysts for the transformation of cyclopentanes [8] results in low yields of aromatic hydrocarbons.

In our previous work [9] it was shown that at 450° and 20 atm over Pt-Al$_2$O$_3$ and Pt-ZrO$_2$ bicyclopentyl is isomerized into the condensed system of decalin with subsequent dehydrogenation to tetralin and naphthalene; scarcely any hydrogenolysis of the C—C bonds of the cyclopentane ring is observed under these conditions. In connection with these results it was of considerable interest to investigate the transformations of cyclopentanes containing longer side chains than ethyl because the results could enable certain conclusions to be drawn about the mechanism of the catalytic transformations of hydrocarbons of higher molecular weight forming components of the gasoline-ligroin fraction used in catalytic reforming.

Our investigation showed that, unlike bicyclopentyl, isopentylcyclopentane readily undergoes hydro-genolysis at all the bonds of the five-membered ring at 450° under a hydrogen pressure of 20 atm in presence of Pt-Al$_2$O$_3$. Hydrogenolysis is accompanied by the formation of aromtic hydrocarbons. It is particularly note-worthy that under these conditions platinum deposited on zirconium oxide brings about scarcely any hydro-genolysis of the cyclopentane ring.

EXPERIMENTAL

The isopentylcyclopentane used was synthesized as indicated below:

451
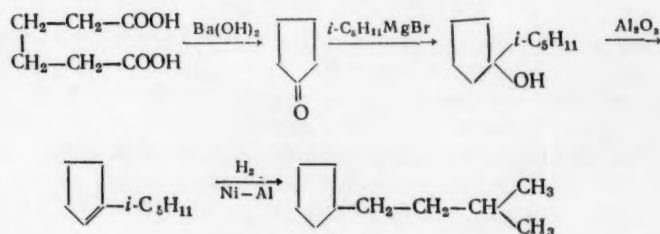
The product was distilled through a column of 70-plate efficiency; it had the following constants: b. p. 171.2° (744 mm); $n^{20}D$ 1.4337 and d^{20}_4 0.7875; found MR 46.34; for $C_{10}H_{20}$, calculated MR 46.38.

1-Isopentyl-1-cyclopentene had: b. p. 168-168.5° (760 mm); $n^{20}D$ 1.4507 and d^{20}_4 0.8151; found MR 45.61; for $C_{10}H_{18}$, calculated MR 45.71.

Raman spectrum of isopentylcyclopentane: $\Delta\nu$ (cm^{-1}): 252(2b), 294 (2b), 406 (2), 509 (0), 799 (1), 823(2), 863 (1), 894 (8b), 955 (5), 977 (1), 1018 (1), 1038 (2), 1057 (1), 1080 (3), 1103 (5b), 1138 (4b), 1170 (4), 1192(4), 1224 (1), 1280 (1), 1297 (5), 1312 (1), 1336 (7b), 1383 (1b), 1433 (8), 1445 (10), 1459 (8), 2845 (8), 2860(10), 2905 (2), 2956 (10), 3040 (9sh), 3065 (1), 3076 (1).

The transformations of isopentylcyclopentane were carried out in presence of platinized alumina and zirconia containing 0.5% of Pt at 450° under a hydrogen pressure of 20 atm at a space velocity of 0.5 hour^{-1} at a molar ratio of hydrogen to hydrocarbon of 4:1. The catalyzates were fractionated through a column, and their compositions were determined by chemical methods and from their Raman spectra.

Transformations of isopentylcyclopentane in presence of platinized alumina. From 78.5 g of isopentyl-cyclopentane passed we obtained 65.6 g (83.6%) of catalyzate with $n^{20}D$ 1.4513 and d^{20}_4 0.7787. The outgoing gases contained 83.7% of hydrogen and 16.3% of saturated hydrocarbons (9.4% CH_4, 2.8% C_2H_6 3.6% C_3H_8, 0.5% C_4H_{10}). By chromatographic adsorption on silica gel we isolated 31.8 g of aromatic hydrocarbons and 32.6 g of a mixture of cycloalkanes and alkanes. Table 1 gives the results of the analytical fractionation of the cycloalkane-alkane part of the catalyzate through a column.

TABLE 1

Fractional Composition of the Cycloalkane-Alkane Part of the Isopentyl-cyclopentane Catalyzate

Fraction	B. p. (°C at 749 mm)	n^{20}_D	d^{20}_4	Yield of fraction (% by wt.)	
				on cyclo-alkane-alkane part	on catalyzate
I	<28.4	1,3500 при 0°	—	7,4	3,6
II	28,4—31	1,3532	—	0,9	0,5
III	31 —33,6	1,3545	0,6224	3,1	1,5
IV	33,6—59	1,3642	—	3,1	1,5
V	59 —61,2	1,3708	0,6542	3,3	1,7
VI	61,2—70	1,3823	0,6778	1,5	0,8
VII	70 —72,8	1,4080	0,7465	4,6	2,8
VIII	72,8—87,6	1,3945	—	4,6	2,8
IX	87,6—89	1,3913	0,6967	2,8	1,4
X	89 —156	1,4045	0,7225	10,7	5,3
XI	156,0	1,4123	0,7364	9,5	4,7
XII	156,0—159	1,4130	—	5,9	2,9
XIII	159 —161,5	1,4133	0,7389	6,1	3,1
XIV	161,5—166	1,4161	0,7437	9,8	4,9
XV	166 —168	1,4263	0,7648	5,8	2,9
XVI	168 —170	1,4322	0,7867	16,0	8,0

Fraction I, which was collected in a trap cooled with solid carbon dioxide, was analyzed on a chromatograph: it contained a mixture of C_4 alkanes and isopentane. Fraction III contained a mixture of pentane and 2-methylbutane. Fraction V consisted mainly of 2-methylpentane. Fraction VII [b. p. 70-72.8° (749 mm), $n^{20}D$ 1.4080 and d^{20}_4 0.7405] consisted mainly of methylcyclopentane. Fraction IX [b. p. 87.6-89°, (749mm), $n^{20}D$ 1.3913 and d^{20}_4 0.6967) probably consisted mainly of 2,3-dimethylpentane. Fraction XI(b. p.156°, (749mm), $n^{20}D$ 1.4123 and d^{20}_4 0.7364) was 2,5-dimethyloctane. For 2,5-dimethyloctane the literature [10] gives b. p. 158° (760 mm), $n^{20}D$ 1.414; d^{20}_4 0.736. Fraction XIII [b. p. 159-161.5° (749 mm); $n^{20}D$ 1.4133 and d^{20}_4 0.7389] was fairly pure 5-ethyl-2-methylheptane. For 5-ethyl-2-methylheptane the literature [10] gives b. p. 159.7° (760 mm); $n^{20}D$ 1.4134 and d^{20}_4 0.736 . The Raman spectra of Fractions XIV and XV showed that they consisted of a mixture of

C$_{10}$ paraffins (mainly 2-methylnonane) together with unchanged isopentylcyclopentane. Fraction XVI contained unchanged isopentylcyclopentane.

The aromatic hydrocarbons were also fractionated through a column into narrow fractions. The results are given in Table 2.

TABLE 2

Fractional Composition of the Aromatic Part of the Isopentylcyclopentane Catalyzate

Fraction	B. p. (°C at 749 mm)	n_D^{20}	d_4^{20}	Yield of fraction (% by wt)	
				on cyclo-alkane-alkane part	on catalyzate
I	81 —110,8	1,4983	0,8725	5,6	2,7
II	110,8—147	1,4947	0,8694	8,5	4,1
III	147 —163	1,4936	0,8656	8,8	4,3
IV	163 —171,6	1,4912	0,8638	11,3	5,5
V	171,6—173	1,4902	0,8634	6,9	3,4
VI	173 —181	1,4917	0,8658	8,5	4,1
VII	181 —185	1,4960	0,8720	19,1	9,3
VIII	185 —187	1,5081	0,8983	15,7	7,6
residue	—	—	—	13,8	6,8

Fraction I contained benzene and toluene. Fraction II was mainly toluene (about 75%) together with some xylenes. The Raman spectrum of the combined Fractions III and IV showed the presence of isobutylbenzene, p-ethyltoluene, cumene, and propylbenzene. The Raman spectrum of the combined Fractions V and VI showed that it consisted of p-propyltoluene, cymene, and isobutylbenzene. Fractions VII and VIII consisted of a mixture of ethylxylenes, the main component of which was 5-ethyl-m-xylene.

The residue (4.4 g) was fractionated from a Favorskii flask with collection of the following fractions:

Fraction I: b. p. 195-200° (750 mm); n^{20}D 1.5280 (2.8 g). Found: C 89.57; 89.78; H 9.52; 9.55%. C$_{10}$H$_{44}$. Calculated: C 89.56; H 9.44%.

Fraction II: b. p. 200-202° (750 mm); n^{20}D 1.5320 (1.2 g). Found: C 90.85; 91.0; H 9.17; 9.18%. C$_{10}$H$_{12}$. Calculated: C 90.85; H 9.15%.

Fraction I was probably a mixture of ethylxylenes and tetramethylbenzenes [11]. The possibility cannot be excluded that the bulk of Fraction II consisted of 5-methylindan [12].

It will be seen from the results that in the catalytic treatment of isopentylcyclopentane hydrogenolysis occurs at all the bonds of the cyclopentane ring with formation of 2,5-dimethyloctane, 5-ethyl-2-methylheptane, and 2-methyloctane. The isoparaffins formed by hydrogenolysis then undergo hydrocracking, mainly in the middle of the molecule, with formation of C$_4$ paraffins, pentane, isopentane, and C$_6$ paraffins:

$$\text{---} \rightarrow CH_3\text{---}CH\text{---}CH_2\text{---}CH_3 + CH_3\text{---}CH_2\text{---}CH_2\text{---}CH_2\text{---}CH_3$$
$$\underset{CH_3}{|}$$

$$\text{---} \rightarrow CH_3\text{---}CH\text{---}CH_3 + CH_3\text{---}CH\text{---}CH_2\text{---}CH_2\text{---}CH_3$$
$$\underset{CH_3}{|} \qquad\qquad \underset{CH_3}{|}$$
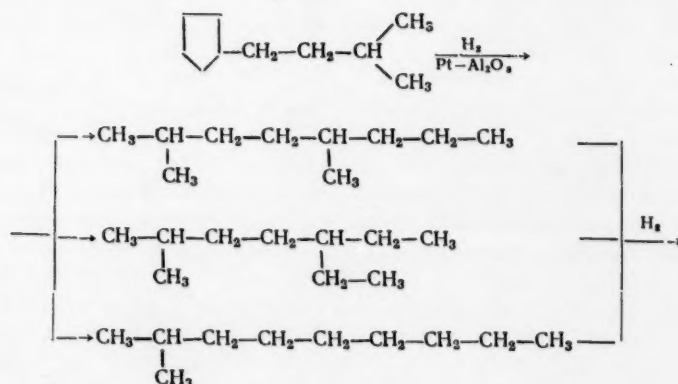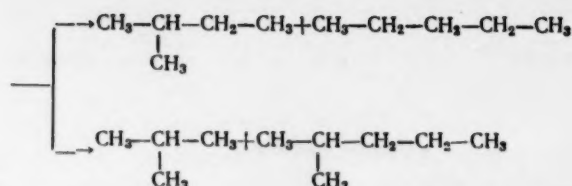
It is known that the place at which cleavage of a C—C bond occurs in an alkane is largely determined by the nature of the catalyst and the reaction conditions. Thus, as we have shown [13], in presence of Raney nickel at 200° the hydrocracking of n-alkanes proceeds only in the direction of the elimination of end methyl groups. Analogous results for branched paraffins were obtained previously by Ipatieff and Haensel [14] in presence of nickel on kieselguhr. Unlike these catalysts, platinum and nickel on acidic carriers (Al_2O_3 [15], Al_2O_3-SiO_2 [16]), bring about the hydrocracking of paraffins with preferential cleavage nearer to the middle of the carbon chain. The hydrogenolysis of isopentylcyclopentane over Pt-Al_2O_3 at 450° and 20 atm is accompanied by transformations into aromatic hydrocarbons: benzene, toluene (about 5%), p-ethyltoluene, propylbenzene, cumene (about 9%), cymene, isobutylbenzene, p-propyltoluene (7.5%), and ethylxylenes (about 20%).

The formation of aromatic hydrocarbons in the catalytic treatment of isopentylcyclopentane may be represented as isomerization of the cyclopentane ring to the cyclohexane ring with subsequent dehydrogenation to isobutylbenzene:
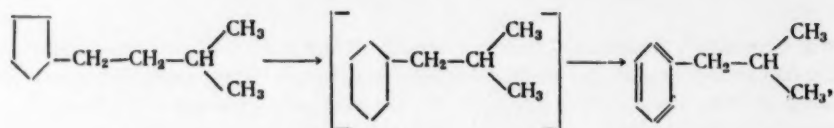
and also as direct closure of a six-membered ring with participation of the carbon atoms of the side chain and formation of hexahydro-5-methylindan with subsequent dehydrogenation and hydrogenolysis of the cyclopentane ring:
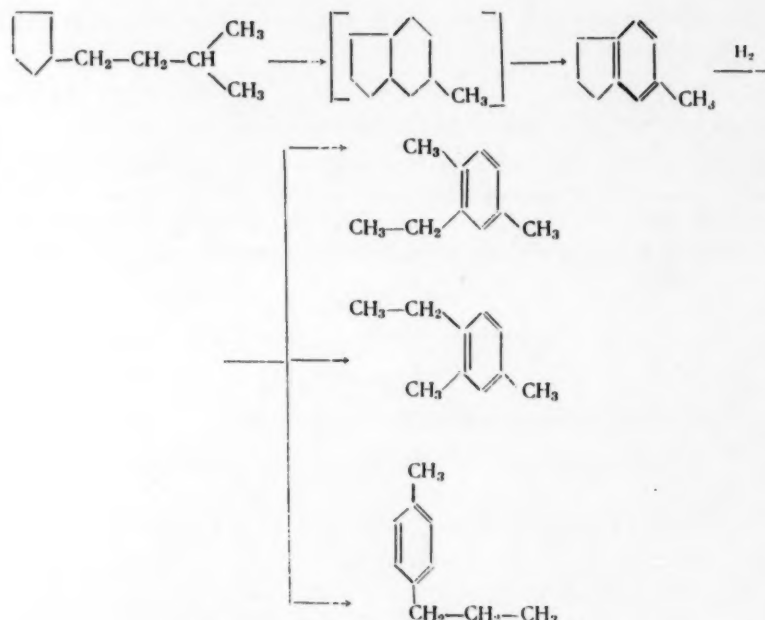
Confirmation of the probability of the second scheme is provided mainly by an examination of the nature of the aromatic hydrocarbons isolated. The aromatic part of the catalyzate consisted mainly of ethylxylenes (about 20%) together with p-propyltoluene and cymene. The formation of the latter in such a relatively large amount is difficult to imagine on the basis of reaction via isobutylbenzene, for it is seen from data in the literature [17] and from data obtained by us [18] that, in presence of acidic catalysts, aromatic hydrocarbons having a long side chain undergo mainly hydrogenolysis of side chains. The proposed scheme for the formation of aromatic hydrocarbons is confirmed also by the nature of the high-boiling part of the catalyzate, which was isolated from the residue by fractionation.

Catalytic treatment of isopentylcyclopentane and 1-isopentyl-1-cyclopentene in presence of platinized zirconia at 450° under a pressure of hydrogen of 20 atm. In the investigation of the catalytic transformations of isopentylcyclopentane over platinized zirconia containing 0.5% of platinum we took 78.5 g of the hydrocarbon. We obtained 71.4 g of catalyzate, $n^{20}D$ 1.4395 and d^{20}_4 0.7953. After separation of the aromatic hydrocarbons (1.7 g), which boiled in the range 120-162° and had $n^{20}D$ 1.4932 and d^{20}_4 0.8674, the naphthene-paraffin part (68.2 g) was fractionated through an efficient column. We isolated 2.6 g of a fraction of b. p. 148-169° (745 mm); $n^{20}D$ 1.4287 and d^{20}_4 0.7779, and also 64.1 g (89.8% on the catalyzate) of unchanged isopentylcyclopentane, which had b. p. 169-170.2° (745 mm); $n^{20}D$ 1.4335 and d^{20}_4 0.7879. Hence, scarcely any hydrogenolysis of the cyclopentane ring of isopentylcyclopentane occurs in presence of platinized zirconia.

We showed previously [18] that Pt-ZrO_2, unlike Pt-Al_2O_3, is a mild dehydrogenating catalyst for cyclohexane compounds. In view of the results of the investigation of the transformations of isopentylcyclopentane in presence of Pt-ZrO_2, it was of interest to study also the behavior of 1-isopentyl-1-cyclopentene under the same conditions. In the experiment we took 59.2 g of hydrocarbon and obtained 57.2 g of catalyzate of $n^{20}D$ 1.4348, which, after separation of the aromatic hydrocarbons (about 1.5% by volume), was distilled through a column; it consisted entirely of isopentylcyclopentane: b. p. 169.5-170.4° (748 mm); $n^{20}D$ 1.4337; d^{20}_4 0.7875.

Hence, the results give us reason to suppose that the carrier has a substantial, and in the present case decisive, effect on the properties of the catalyst: Pt-ZrO_2 was found to be almost completely inactive both in the hydrogenolysis and in the isomerization of the cyclopentane ring, while fully preserving its hydrogenating power toward an ethylenic bond.

SUMMARY

1. A study was made of the catalytic transformations of isopentylcyclopentane in presence of Pt-Al_2O_3 and Pt-ZrO_2 at 450° under a pressure of hydrogen of 20 atm.

2. In presence of platinized alumina isopentylcyclopentane reacts with formation not only of products of the hydrogenolysis of the cyclopentane ring (2,5-dimethyloctane, 5-ethyl-2-methylheptane, and 2-methylnonane), but also of a considerable amount of aromatic hydrocarbons. In this case the latter are formed not only by isomerization of the cyclopentane ring to a cyclohexane ring with subsequent dehydrogenation, but also by direct closure of a six-membered ring, with participation of carbon atoms of the side chain, with formation of a hexahydroindan system, which undergoes dehydrogenation in the six-membered ring and hydrogenolysis in the five-membered ring.

3. Under the conditions studied Pt-ZrO_2 brings about scarcely any hydrogenolysis of the cyclopentane ring, but is a hydrogenating catalyst for a double bond in the ring.

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PREPARATION OF AROMATIC HYDROCARBONS FROM TUIMAZIN
GASOLINE BY TWO-STAGE AROMATIZATION

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Aromatic hydrocarbons are of exceptionally high importance for the national economy. Thus, they form a valuable raw material for various branches of chemical industry. In this connection the question of the technical preparation of aromatic hydrocarbons, in particular toluene and xylenes, from petroleums of the Volga-Urals groups is a very pressing one. Essentially, the methods of aromatizing hydrocarbons consist in the dehydrogenation of cyclohexanes [1-4], the dehydrocyclization of paraffins [5-8], and the dehydroisomerization of cyclopentane homologs [9-15]. The results of the investigations cited have formed the basis of modern methods of catalytic reforming and aromatization of petroleum distillates.

The object of the present work was the determination of the possibility of preparing toluene and xylenes from low-octane Tuimazin gasoline by the two-stage aromatization of the heptane-methylcyclohexane (b. p. 91-103°) and octane-dimethylcyclohexane (b. p. 117-127°) fractions of Tuimazin gasoline. This method permits a substantial increase in the amount of aromatic hydrocarbons in the gasolines not only by the dehydrogenation of the cyclohexanes present, but also by the isomerization of cyclopentanes into cyclohexanes in presence of anhydrous aluminum chloride and subsequent dehydrogenation of the newly formed cyclohexanes in accordance with the scheme below.
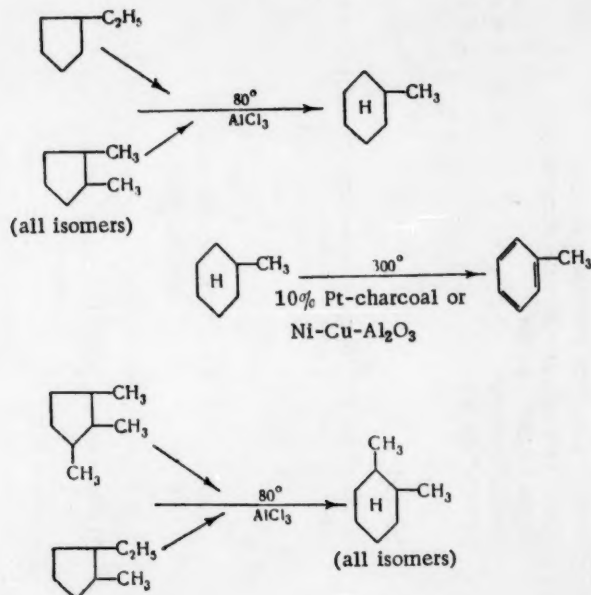
TABLE 1

Properties of the Original Tuimazin Gasoline and of the Narrow Fractions Separated from It

Boiling range of gasoline or of fraction separated from it	$n^{20}D$	d^{20}_4	Aromatics content (% by vol.)	Sulfur content (% by wt.)	Octane rating		Yield (% by wt.)	
					In pure state (no $PbEt_4$)	with 1.5 ml of $PbEt_4$	on whole gasoline	on petroleum
34–200°: the whole Tuimazin gasoline	1.4103	0.7305	8.0	0.08	37.5	59.6	–	25.0
Whole Tuimazin gasoline after removal of the 91–103° fraction	1.4122	0.7332	7.5	0.08	40.0	60.0	–	–
91–103° fraction	1.4012	0.7165	5.0	0.014	–	–	10.0	2.5
117–127° fraction	1.4133	0.7350	8.0	0.015	–	–	8.0	~20

TABLE 2

Results of the Two-Stage Aromatization of Unfractionated Tuimazin and Its Narrow Fractions

Catalyst	Product subjected to aromatization	after dehydrogenation without preliminary treatment with AlCl₃			Properties of catalyzate			octane rating	
					after treatment with AlCl₃ and dehydrogenation				
		$n^{20}D$	d^{20}_4	aromatics content (% by vol.)	$n^{20}D$	d^{20}_4	aromatics content (% by vol.)	in pure state (no $PbEt_4$)	with 1.5 ml of $PbEt_4$
Pt-charcoal	91–103° fraction of Tuimazin gasoline	1.4198	0.7308	25.5	1.4210	0.7381	30.0	–	–
Ni–Cu–Al₂O₃	The same	1.4195	0.7305	25.5	1.4202	0.7325	27.5	–	–
Ni–Cu–Al₂O₃	117–127° fraction of Tuimazin gasoline	1.4161	0.7427	16.0	1.4325	0.7652	33.0	–	–
Ni–Cu–Al₂O₃	Whole Tuimazin gasoline	1.4195	0.7460	22.0	–	–	–	41.0	66.0
Ni–Cu–Al₂O₃	The same	–	–	–	1.4272	0.7380	29.0	44.0	68.0
Ni–Cu–Al₂O₃	Whole Tuimazin gasoline after removal of the 91–103° fraction	–	–	–	1.4234	0.7523	22.0	48.0	67.0

$$\text{CH}_3 \text{ (cyclohexane with CH}_3, \text{ H)} \xrightarrow[\substack{10\% \text{ Pt-charcoal or} \\ \text{Ni-Cu-Al}_2\text{O}_3}]{300°} \text{CH}_3 \text{ (xylene)}$$
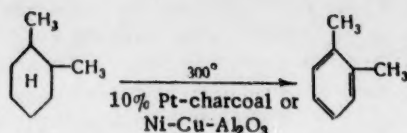
In view of the fact that in the preparation of toluene by this method a fraction is collected over the range 91-103° which amounts to 10% of the original gasoline, it was of interest to investigate also the motor-fuel properties of the residue (head and tail parts) of the gasoline after separation of the 91-103° fraction. It was found that the octane rating of the combined residue (head and tail parts) was scarcely any lower; when determined in absence of tetraethyllead it was even higher by 2.5 points, probably because of the removal of one of the detonating centers, heptane.

In the solution of our problem we made use of the catalytic dehydrogenation of cyclohexanes with preliminary isomerization of cyclopentanes into cyclohexanes in presence of aluminum chloride. During treatment with the latter the isomerization of cyclopentanes into cyclohexanes was accompanied by almost complete desulfurization of the gasoline fraction. For the dehydrogenation we used platinized charcoal containing 10% of finely dispersed platinum and a nickel-copper-alumina catalyst of composition 67.5% Ni + 2.5% Cu + 30% Al_2O_3. The experiments showed that by the aromatization of the 91-103° fraction of Tuimazin gasoline in presence of either platinized charcoal or of the nickel-copper-alumina catalyst its toluene content can be increased from 5% to 25.5%, the content depending on the extent of dehydrogenation. Also, when the cyclopentanes are isomerized to cyclohexanes, the toluene content of the fraction can be increased further by 4.5%, i.e., to 30% by volume.

By the two-stage aromatization of the octane-dimethylcyclohexane fraction (b. p. 117-127°) of Tuimazin gasoline the content of aromatic hydrocarbons can be increased, mainly at the expense of dimethylcyclohexanes, from 8% to 33% by volume. The isomerization of cyclopentanes to cyclohexanes accounts for an increase in xylene content of 17%.

EXPERIMENTAL

The fractions for investigation were separated from Tuimazin gasoline by fractionation through à column of 19-plate efficiency. The properties of the original gasoline and the fractions separated from it are given in Table 1.

Isomerization of cyclopentanes to cyclohexanes in presence of aluminum chloride. The isomerization was carried out in a three-necked flask fitted with mechanical stirrer, thermometer, and condenser. The condenser was connected to a trap cooled with solid carbon dioxide. In the isomerization experiments the temperature did not exceed 80°. Each experiment lasted for eight hours. The amount of aluminum chloride taken was 5% on the weight of the original gasoline. The loss of gasoline in the experiment did not exceed 3%. At the end of the catalytic treatment the gasoline was separated from the aluminum chloride, washed with water, with dilute sodium carbonate solution, and again with water until neutral, and dried with calcium chloride: it was distilled through the 19-plate column.

Dehydrogenation of the whole Tuimazin gasoline and of the narrow fractions separated from it. The dehydrogenation experiments were carried out in the usual laboratory flow-type apparatus. The catalysts were platinized charcoal containing 10% of finely dispersed platinum and a nickel-copper-alumina catalyst of the following composition: 67.5% Ni + 2.5% Cu + 30% Al_2O_3. After reduction the catalyst occupied a volume of 100 ml. Gasoline was fed into the tube containing the catalyst at a space velocity of 0.5 hour^{-1} in 50 ml portions. Refractive index, content of aromatic hydrocarbons (by the sulfuric acid method), and specific gravity were determined on the catalyzates obtained. The activities of the catalyzates were checked before and after the experiments by passage of a little (5 ml) cyclohexane and determination of the extent of dehydrogenation (%) from the refractive index of the resulting catalyzate. The octane rating of the gasoline was determined in a Waukesha engine. The results of the two-stage aromatization of the heptane-methylcyclohexane and the octane-dimethylcyclohexane fractions, and also of the unfractionated Tuimazin gasoline and the residue remaining from this after removal of the 91-103° fraction, are given in Table 2. The variations in the activities of the catalysts with time in the course of experiments on dehydrogenation are shown in Figs. 1 and 2.
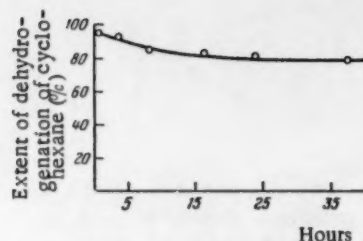
Fig. 1. Variation of the activity of 10% Pt-charcoal with time in the dehydrogenation of the 91-103° fraction of Tuimazin gasoline. Control experiments with cyclohexane.
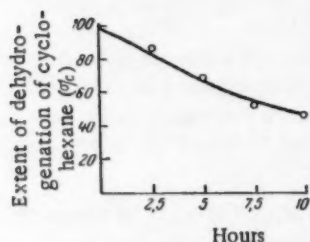

Fig. 2. Variation of the activity of a nickel-copper-alumina catalyst with time in the dehydrogenation of the 91-103° fraction of Tuimazin gasoline. Control experiments with cyclohexane.

We found that aluminum chloride treatment of a sample of gasoline from which the 91-103° fraction had been removed did not affect its octane rating of 40. However, after the addition of 1.5 ml of tetraethyllead to the samples the octane rating of the $AlCl_3$-treated sample was 63.4, as against 60 before the aluminum chloride treatment.

It follows from Table 2 that use of the method of dehydrogenational catalysis can increase the toluene content of the 91-103° fraction from 5% to 25.5%, i.e., by 20.5% by volume, and that of the 117-127° fraction from 8% to 16%, i.e., it can be doubled. By isomerization of the cyclopentanes (treatment with $AlCl_3$) the toluene content of the catalyzate of the 91-103° fraction can be further increased by 4.5%, i.e., to 30%, and the xylene content of the catalyzate of the 117-127° fraction can be increased to 33%, which is an increase of 17%. Also, the experiments showed that after the removal of the heptane-methylcyclohexane fraction from Tuimazin gasoline the motor-fuel properties were not worsened (see octane ratings in Table 1).

Comparison of the results on the operation of the catalysts given in Figs. 1 and 2 shows that both the nickel-copper-alumina catalyst and the platinum catalyst can be used for the dehydrogenation of cyclohexanes. However, the nickel-copper-alumina catalyst is not as stable as the platinum catalyst. After ten hours of work the nickel-copper-alumina catalyst suffers a sharp fall in activity in dehydrogenation experiments (in this time 498 ml of gasoline is passed). Under the same conditions the platinum catalyst brought about the aromatization of the gasoline over a period of 37.5 hours, and during this time its activity remained almost constant. However, a spent nickel-copper-alumina catalyst can be readily regenerated by oxidation with air at 300° for 4-5 hours and subsequent reduction with hydrogen at 350°. After regeneration this catalyst again acquires high activity (extent of dehydrogenation of cyclohexane 95-90%).

SUMMARY

1. By two-stage aromatization of the heptane-methylcyclohexane fraction of Tuimazin gasoline in presence of platinized charcoal (10% Pt) its toluene content can be raised from 5 to 30% by volume.

2. Like the platinum catalyst, a nickel-copper-alumina catalyst (67.5% Ni + 2.5% Cu + 30% Al_2O_3) can be used for the dehydrogenation of cyclohexanes. It is less stable than the platinum catalyst, but it can be regenerated in situ.

3. By two-stage aromatization of the octane-dimethylcyclohexane fraction of Tuimazin gasoline in presence of a nickel-copper-alumina catalyst its aromatics (mainly xylene) content can be raised from 8 to 33% by volume. Here the preliminary isomerization of cyclopentanes to cyclohexanes in presence of aluminum chloride accounts for 17% increase in the xylene content.

4. Removal of the 91-103° fraction from the whole Tuimazin gasoline does not lower its octane rating.

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DETERMINATION OF THE INDIVIDUAL HYDROCARBON
COMPOSITIONS OF GASOLINES OF TATAR PETROLEUMS

COMMUNICATION 3. GASOLINES FROM PETROLEUMS FROM DIFFERENT LEVELS

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In previous communications [1] data were presented on the individual hydrocarbon compositions of gasolines of petroleums drawn from the first D_I Devonian horizon in various Tatar petroleum deposits. In the present work we investigated three gasolines from petroleums from different Devonian and Carboniferous horizons: coal-bearing formations (C_I^{2h}, Boring 426) from the Bablin site, a Kyn layer (D_0, Boring 616), and a Givetian deposit (D_{III}, Boring 641) from the Romashka site. The investigation was carried out by Kazanskii and Landsberg's method [2], which we used also in the previous investigations [1, 3]. The group compositions, in which normal and branched paraffins and also cyclopentanes, cyclohexanes, and aromatics are considered separately (the gaseous hydrocarbons are not taken into account), are given in Table 1.

TABLE 1

Group of hydrocarbons	Content (% by wt. on gasoline		
	Carboniferous C_I^{2h}	Devonian D_0	Devonian D_{III}
Normal paraffins	29.0	27.9	27.3
Branched paraffins	35.1	30.9	23.5
Cyclopentanes	7.9	8.8	7.2
Cyclohexanes	8.6	10.0	13.5
Aromatics	2.2	3.7	5.9

It will be seen from Table 1 that the content of cyclohexanes and aromatics increases as we pass from the higher to the lower horizons, whereas there is no such regularity in the variation in the content of cyclopentanes.

A certain dependence on sulfur content extends here even to the distribution of paraffins. With increase of the sulfur content of the petroleum there is an increase in the over-all content of paraffins in the gasolines with a simultaneous relative increase in the content of branched paraffins as compared with normal paraffins. Andreev and Ivanova [4] point out the part played by sulfur in the transformations of petroleum in nature. Hydrogen sulfide formed during the action of sulfur may hydrogenate naphthenes with ring-opening and formation of paraffins. It is known also that the hydrogenation of, e.g., substituted cyclopentanes leads mainly to the formation of isoparaffins, rather than normal paraffins [5]. The relative increase in the amount of isoparaffins, as compared with that of normal paraffins, may be partly explained in this way.

TABLE 2

Hydrocarbon	Content (% by wt. on gasoline)			Hydrocarbon	Content (% by wt. on gasoline)		
	Carboniferous C_I^{2h}	Devonian D_0	Devonian D_{III}		Carboniferous C_I^{2h}	Devonian D_0	Devonian D_{III}
Paraffins				Propylcyclopentane	0.15	0.13	0.17
				Isopropylcyclopentane	+	0.30	0.16
Pentane	5.20	5.96	3.04	1-cis-Ethyl-2,4-cis-trans-dimethylcyclopentane	0.14	0.13	0.16
2-Methylbutane	3.52	3.23	1.50				
Neopentane	–	–	–				
Hexane	6.12	5.74	6.40	Total	6.82	7.65	7.72
2-Methylpentane	4.77	4.78	3.54				
3-Methylpentane	3.21	2.91	1.93	**Cyclohexanes**			
2,2-Dimethylbutane	0.20	0.06	0.04				
2,3-Dimethylbutane	0.40	0.45	0.20				
Heptane	7.08	5.85	8.11	Cyclohexane	0.75	0.61	1.88
2-Methylhexane	2.21	1.68	1.78	Methylcyclohexane	2.43	2.14	4.43
3-Methylhexane	4.28	3.57	2.98	1,1-Dimethylcyclohexane	0.14	0.46	0.23
2,2-Dimethylpentane	0.11	0.10	0.24	1,2-Dimethylcyclohexane	0.31	0.43	0.52
2,3-Dimethylpentane	0.83	1.19	0.62	1,3-Dimethylcyclohexane	0.69	0.91	1.44
2,4-Dimethylpentane	0.23	0.10	0.24	1,4-Dimethylcyclohexane	0.42	0.53	0.54
3-Ethylpentane	0.50	0.36	0.51	Ethylcyclohexane	0.93	0.91	1.47
Octane	5.78	5.68	8.49	Propylcyclohexane	0.07	0.10	0.11
2-Methylheptane	2.79	2.68	2.82	Isopropylcyclohexane	0.06	0.07	0.11
3-Methylheptane	1.08	1.01	0.92	1-Ethyl-2-methylcyclohexane	0.09	0.12	0.24
4-Methylheptane	0.94	0.56	0.58	1-Ethyl-3-methylcyclohexane	0.18	0.25	0.45
2,3-Dimethylhexane	0.83	0.46	0.50	1-Ethyl-4-methylcyclohexane	0.09	0.12	0.21
2,4-Dimethylhexane	0.82	0.68	0.91	1,1,2-Trimethylcyclohexane	+	0.10	0.29
Nonane	0.93	1.02	1.25	1,1,3-Trimethylcyclohexane	1.03	1.51	1.05
2-Methyloctane	0.72	0.60	0.72	1,1,4-Trimethylcyclohexane	0.16	0.32	0.20
3-Methyloctane	0.96	0.60	0.72	1,2,3-Trimethylcyclohexane	–	–	–
4-Methyloctane	0.79	0.89	1.02	1,2,4-Trimethylcyclohexane	0.06	0.08	0.15
2,3,5-Trimethylhexane	0.09	0.13	0.48	1,3,5-Trimethylcyclohexane	0.04	0.04	0.14
2,6-Dimethylheptane	0.78	0.58	0.88	Total	7.45	8.70	13.46
4-Ethylheptane	+	+	0.07				
2,3-Dimethylheptane	0.31	0.23	0.14	**Aromatics**			
3-Ethyl-3-methylhexane	–	–	0.14				
Gas (not analyzed)	13.47	13.3	0.40*				
Total	63.95	64.23	51.17	Benzene	0.20	0.37	0.49
				Toluene	0.68	1.09	1.79
Cyclopentanes				Ethylbenzene	0.31	0.63	1.26
Cyclopentane	0.28	0.42	0.32				
Methylcyclopentane	1.53	1.18	1.58				
cis-1,2-Dimethylcyclopentane	0.31	0.27	0.35				
trans-1,2-Dimethylcyclopentane	0.92	1.29	1.12				
cis-1,3-Dimethylcyclopentane	0.42	0.39	0.31				

* The gasoline was first debutanized.

TABLE 2 (continued)

Hydrocarbon	Content (% by wt. on gasoline)			Hydrocarbon	Content (% by wt. on gasoline)		
	Carbon-iferous C_I^{2h}	Devonian D_0	Devonian D_{III}		Carbon-iferous C_I^{2h}	Devonian D_0	Devonian D_{III}
trans-1,3-Dimethylcyclo-pentane	0.42	0.39	0.31	o-Xylene	0.13	0.18	0.36
Ethylcyclopentane	0.54	0.64	0.77	m-Xylene	0.42	0.72	1.45
1,2,3-cis-cis-cis-Trimethyl-cyclopentane	0.27	0.36	0.19	p-Xylene	0.18	0.26	0.54
1,2,3-cis-trans-cis-Trimethyl-cyclopentane	0.52	0.45	0.42	Total	1.92	3.25	5.89
1,2,4-cis-trans-cis-Trimethyl-cyclopentane	0.52	0.45	0.42	Accounted for and identified	85.14	83.83	78.24
1,2,4-cis-cis-trans-Trimethyl-cyclopentane	0.63	0.83	0.69	Unaccounted for	6.02	5.35	4.69
1-Methyl-3-propylcyclo-pentane	0.17	0.42	0.50	Residue in distillation flasks	2.72	4.71	4.68
				Losses	6.12	6.11	12.39

The distribution of the individual hydrocarbons in these gasolines is shown in Table 2.

Comparison of the data in Table 2 shows that in all the gasolines, hydrocarbons containing one tertiary carbon atom in the chain predominate among the branched paraffins. It is found that hydrocarbons containing an odd number of carbon atoms in a straight chain generally have the CH_3 group on the second carbon atom, whereas hydrocarbons containing an even number of carbons in the chain have the CH_3 group on the third carbon atom. Among the cyclohexanes there is a definite regularity in the distribution of individual hydrocarbons, e.g., 1,3-dimethylcyclohexane > 1,4-dimethylcyclohexane > 1,2-dimethylcyclohexane. There is an analogous regularity for xylenes and gem-disubstituted cyclohexanes (1,1,3-, 1,1,4-, and 1,1,2-trimethylcyclohexanes).

SUMMARY

1. An investigation was made of three gasolines from Tatar petroleums from different Devonian and Carboniferous horizons having an upper boiling limit of 150°.

2. The relation of the group hydrocarbon composition to the total sulfur content of the petroleum is shown.

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HOMOGENEOUS DESTRUCTIVE HYDROGENATION OF CRESOLS
AT HIGH PRESSURES OF HYDROGEN

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Fischer and Tropsch [1], in an investigation of the berginization of the three isomeric cresols at 460° at
an initial hydrogen pressure of 95 atm, observed partial elimination of a methyl group with formation of phenol.
Later, Hagemann and Neuhous [2] found that in the destructive hydrogenation of high-boiling phenols in pres-
ence of Fe_2O_3 or Al_2O_3 low-boiling phenols are formed. Cawley [3] (1933) investigated the homogeneous destructive
hydrogenation of m-cresol (in absence of catalysts) at 500° at an initial hydrogen pressure of 100 atm for two
hours. Under these conditions the author obtained 24% by weight of phenol, 21% by weight of aromatic hydro-
carbons, and 6% by weight of water (on the amount of cresol taken). A paper by Kalechits and Salingareeva [4]
gives data on the destructive hydrogenation of cresols at 478° at a hydrogen pressure of 370 atm in presence of
an iron catalyst. The amounts of phenol obtained were about 12% from m-cresol, about 16% from o-cresol, and
about 18% from p-cresol (the yields of neutral products were 33.7%, 37.5%, and 43.3%, respectively). While
the present investigation was in progress, a paper was published by Ielinek [5], who carried out experiments in
a flow apparatus at 600° under a hydrogen pressure of 70 atm (molar ratio of hydrogen to cresol of 1:1). In
absence of catalyst the author obtained 17.6 moles percent of phenol, and in presence of silica gel as catalyst
he obtained 28.0 moles percent of phenol (on the amount of p-cresol taken).

The present work, which forms a continuation of investigations on the homogeneous destructive hydro-
genation of aromatic hydrocarbons and their derivatives [6, 7], had the object of studying the transformations of o-,
m-, and p-cresols in absence of catalyst under high pressures of hydrogen.

EXPERIMENTAL

The experiments were carried out in a 120 ml stainless steel reactor having a hydraulic seal. In each ex-
periment 40 g of the cresol under investigation was placed in the reactor. The cresols were first distilled through
a column of 25-plate efficiency and then had the following constants: o-cresol, b. p. 191.3-191.5° (760 mm) and
$n^{20}D$ 1.5454; m-cresol, b. p. 202.6-202.8° (760 mm) and $n^{20}D$ 1.5398; p-cresol, b. p. 202.2-202.4° (760 mm) and
$n^{20}D$ 1.5394. Initial hydrogen pressures varied from 100 to 300 atm in the various experiments (the working pres-
sures varied correspondingly from 260 to 650 atm). The reactor was heated to the required temperature over a
period of 90 minutes, after which the temperature was kept constant within ± 2° for three hours. When the reactor
was cool, the pressure was gradually lowered to atmospheric; the liquid products were collected in a cooled trap.
The reactor was then rinsed out with ether, and the ethereal solution and liquid products were combined and dried
with anhydrous sodium sulfate. The liquid reaction products were fractionated through the 25-plate column; when the
ether had been removed, we collected the following fractions: Fraction I, b. p. 60.0-95.0°; Fraction II, b. p. 95.0-
113.0°; Fraction III, b. p. 113.0-175.0°; Fraction IV, b. p. 175.0-192.0°; * Fraction V, b. p. 192.0-203.0°.*

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* In the case of o-cresol: Fraction IV, b. p. 175.1-186.5°; Fraction V, b. p. 186.5-192.0°.

TABLE 1

Homogeneous Destructive Hydrogenation of Toluene and Phenol at 490° under Various Initial Pressures of Hydrogen for Three Hours

Initial hydrogen pressure (atm)	Yield of benzene fraction (% by wt.)	
	from toluene	from phenol
100	19.2	8.9
200	33.4	16.4
300	46.0	24.6

Fraction I consisted mainly of benzene; about 85% of this fraction had b. p. 75-95° (n^{20}D 1.4812-1.4872). Refractionation of Fraction I followed by chromatographic separation on silica gel gave a cyclohexane fraction of n^{20}D 1.4264. Fraction II (n^{20}D 1.4920-1.4960) contained toluene. Fraction III (n^{20}D 1.4941-1.4973) was an intermediate fraction. Fraction IV contained phenol and a little unchanged cresol. Fraction V was unchanged cresol containing a little phenol.

The high-boiling residues were investigated separately. The CO and CO_2 contents of the gaseous products were determined; their hydrogen and hydrocarbon contents were determined by chromatographic separation. As well as carrying out the experiments on the homogeneous destructive hydrogenation of cresols, we investigated the behavior of phenol and toluene under the same conditions. This investigation had the object of comparing the rates of elimination of hydroxy and methyl groups from the benzene nucleus during homogeneous destructive hydrogenation. The substances used had the following constants: phenol, b. p. 181.8-182.0° (760 mm); toluene, b. p. 110.8°; n^{20}D 1.4968. In each experiment 40 g of the substance was placed in the reactor. The experimental procedure was the same as for the cresols.[*] As the benzene fraction we took the fraction of b. p. 60-83° in the experiments with phenol and the fraction boiling up to 83° (start of boiling not below 77.5°) in the experiments with toluene.

Comparison of the rates of the demethylation of toluene and dehydroxylation of phenol. We carried out the experiments with phenol and toluene at 490° and at initial hydrogen pressures of 100, 200, and 300 atm. It follows from the results of these experiments (Table 1) that the elimination of the methyl group from toluene occurs about twice as fast as the dehydroxylation of phenol.

Table 1 shows that increase in hydrogen pressure considerably accelerates both of the processes studied. The results lead us to suppose that, under the conditions of homogeneous destructive hydrogenation, it is possible to effect the demethylation of cresols with yields of phenol exceeding the yields of toluene and benzene.

Effect of temperature on the homogeneous destructive hydrogenation of cresol. Table 2 gives the results of experiments with o-cresol at 460°, 475°, and 490° under an initial hydrogen pressure of 300 atm (duration of experiment, three hours).

Table 2 shows that, under the given conditions, the yield of the phenol fraction (Fraction IV) already attains 15.3% by weight on the original cresol (about 35% by weight or 40 moles percent on the cresol that reacted) at 460°. Rise in temperature to 475° and 490° leads to increase in the yield of phenol to 21.6 and 30.0% by weight, respectively, on the original cresol (38 and 33% by weight or 41 and 47 moles percent on the cresol that reacted). The over-all yield of benzene (Fraction I) and toluene (Fraction II) rises from 8.5% by weight on the original cresol at 460° to 27.2% by weight at 490° (19.3 to 30.0% by weight or 23.3 to 38.4 moles percent on the cresol that reacted). The results indicate the possibility of obtaining considerable yields of phenol in the homogeneous destructive hydrogenation of o-cresol. Further experiments with o-, m-, and p-cresols were carried out at 490°.

Effect of hydrogen pressure on the homogenous destructive hydrogenation of cresols. The results of experiments on the homogeneous destructive hydrogenation of o-, m-, and p-cresols at 490° are given in Table 3.

An examination of Table 3 enables us to draw the following conclusions: 1) in experiments with o-cresol the maximum yield of phenol (about 30% by weight on the original phenol) is already attained at an initial hydrogen pressure of 200 atm. Further increase results only in increased yields of benzene and toluene; 2) the homogeneous destructive hydrogenation of m-cresol is much slower than that of o-cresol. The yield of phenol is approximately doubled when the initial hydrogen pressure is increased from 100 to 300 atm. Over this range of pressures the over-all yield of benzene and toluene is more than doubled (almost trebled when calculated in moles percent); 3) at an initial hydrogen pressure of 100 atm the yield of phenol from p-cresol is somewhat less

[*] In the experiments with toluene it was not necessary to rinse out the reactor with ether.

TABLE 2

Homogeneous Destructive Hydrogenation of o-Cresol at an Initial Hydrogen Pressure of 300 atm at Various Temperatures for Three Hours

Temp. (°C)	Yield of liquid products other than water (% by wt. on cresol taken)						
	in all	Fraction I 60—95°	Fraction II 95—113°	Frac. III 113—175°	Fraction IV 175—186.5°	Fraction V 186.5—192	Residue
460	88,4	1,2	7,3	2,4	15,3	56,0	6,2
475	84,7	2,9	8,8	2,2	21,6	43,2	6,0
490	78,0	13,5	13,7	4,1	30,0	9,4	7,3

than from o-cresol, but considerably greater than from m-cresol. When the pressure is raised from 200 to 300 atm there is scarcely any rise in the yield of phenol. There is a simultaneous rise in the yield of benzene and toluene, which, however, is much slower than in the case of o-cresol; 4) the over-all conversion of p-cresol at 300 atm (81.3%) is close to the conversion of o-cresol at 200 atm (79.9%). However, under these conditions the over-all yield of liquid products is considerably higher in the case of o-cresol. From this we may conclude that the observed side reaction of cleavage of the aromatic nucleus with formation of carbon monoxide and paraffins which occurs during the homogeneous destructive hydrogenation of phenols proceeds more vigorously with p-cresol than with o-cresol. This view was later confirmed by the analysis of the gaseous reaction products.

Investigation of the high-boiling reaction products. Fractionation residues from the experiments with o-cresol were combined and redistilled through a column. In the 201.5-202.4° (760 mm) fraction we identified p-cresol in the form of (p-tolyloxy)acetic acid, m. p. 135.5-136°. From the 209-215° (760 mm) fraction we isolated 2,5-xylenol in the form of (2,5-xylyloxy)acetic acid, m. p. 117-118°. In the 215-222.2° (760 mm) fraction we identified p-ethylphenol in the form of (p-ethylphenoxy)acetic acid, m. p. 95-96°.

From the residue remaining after the fractionation we isolated anthracene, m. p. 211-212°. Found: C 94.42; H 5.73%. $C_{14}H_{10}$. Calculated: C 94.38; H 5.61%.

A mixture test with pure anthracene showed no depression of melting point.

Fractionation residues from the experiments with m-cresol were combined and vacuum-distilled from a Claisen flask. In the fraction of b. p. 85-120° (10 mm) we identified 3,5-xylenol in the form of (3,5-xylyloxy)-acetic acid, m. p. 85-86°, and also p-cresol in the form of (p-tolyloxy)acetic acid, m. p. 135.5-136°. These two acids were separated by taking advantage of their different solubilities in hexane. The fraction of b. p. 153-155° (10 mm) appeared to contain phenyl o-tolyl ether. For this the literature gives b. p. 274° (735 mm). Found: C 84.26; H 6.90%. $C_{13}H_{12}O$. Calculated: C 84.7; H 6.52%.

Fractionation residues from the experiments with p-cresol were combined and vacuum-distilled from a Claisen flask. In the fraction of b. p. 110-130° (20 mm) we identified 2,5-xylenol in the form of (2,5-xylyloxy)-acetic acid, m. p. 117-118°. A mixture test with the (2,5-xylyloxy)acetic acid obtained in the experiments with o-cresol showed no depression of melting point. The fraction of b. p. 177-179° (16 mm) appeared to contain bis-p-tolyl ether. Found: C 85.17; H 6.77%. $C_{14}H_{14}O$. Calculated: C 84.85; H 7.06%.

Composition of gaseous reaction products. Data on the compositions of the gaseous products of the homogeneous destructive hydrogenation of o-, m-, and p-cresols at 490° at an initial hydrogen pressure of 300 atm and a reaction time of three hours are given in Table 4.

It may be concluded from Table 4 that the breakdown of the aromatic ring with formation of carbon monoxide and lower hydrocarbons proceeds most vigorously in the case of p-cresol. The possibility cannot be excluded that the carbon monoxide formed undergoes further transformations, not only into CO_2 as a result of reaction with steam, but also to some extent into hydrocarbons. It was therefore of interest to estimate the extent of the breakdown of the aromatic ring also from the composition of the hydrocarbon part of the gaseous products, account being taken of the methane formed by the demethylation of cresol and toluene. Some inaccuracy in this calculation is associated with the fact that benzene is formed not only from toluene, but also from phenol.

TABLE 3

Homogeneous Destructive Hydrogenation of Cresols at Various Initial Hydrogen Pressures (490°, three hours)

Initial hydrogen pressure (atm)	Yield of liquid products other than water (% by wt on cresol taken)						
	in all	Frac. I 60—95°	Frac. II 95—113°	Frac. III 113—175°	Frac. IV* 175—192°	Frac. V* 192—202,8°	Residue
				o-Cresol			
100	87,4	2,9	8,1	3,8	22,6	40,0	10,0
100	87,2	2,0	7,7	4,7	23,8	38,9	10,1
200	81,7	6,2	11,5	3,4	28,7	21,4	10,5
200	81,3	7,3	12,5	4,5	29,6	18,8	8,1
300	74,9	14,2	13,4	3,3	29,8	8,4	5,8
300	78,0	13,5	13,7	4,1	30,0	9,4	7,3
				m-Cresol			
100	88,3	0,7	6,2	2,6	9,6	59,0	10,7
100	88,9	0,7	5,9	1,7	9,6	61,0	10,0
200	86,5	2,9	7,1	2,3	13,3	50,6	10,3
200	84,3	2,6	7,8	1,9	12,0	51,1	8,9
300	76,7	7,1	10,5	2,2	17,4	27,8	11,7
300	76,7	7,0	11,0	2,2	17,6	27,5	11,4
				p-Cresol			
100	85,5	1,5	5,8	6,0	19,8	41,9	10,5
100	84,4	1,4	5,9	6,2	20,0	40,9	10,0
200	76,5	5,8	9,0	4,9	21,5	25,0	10,0
200	76,4	6,1	9,8	4,7	21,0	26,2	8,9
300	71,6	8,2	9,5	4,4	21,3	19,0	9,2
300	69,8	8,9	9,6	4,2	21,0	18,5	7,6

* In experiments with o-cresol: Fraction IV had b. p. 175-186,5° and Fraction V had b. p. 186,5-192°.

If it is assumed that one-half of the benzene formed arises from toluene, then the error in the calculation of the amount of methane does not exceed 1% by weight on the original cresol.*

The results of the calculation (% by weight on original cresol) are given below:

	o-Cresol	m-Cresol	p-Cresol
Total gaseous products	11,5	10,6	13,2
Amounts of these formed in the demethylation of			
cresol	5,1	2,6	3,7
toluene	1,4	0,7	0,9
Gaseous decomposition products	5,0	7,3	8,6

TABLE 4

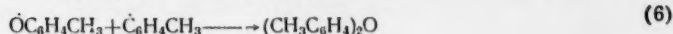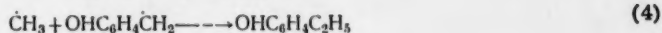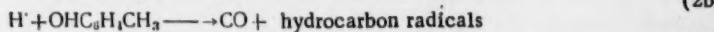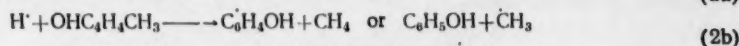Compositions of Gaseous Reaction Products (% by volume)

Original cresol	H_2	CH_4	C_2H_6	C_3H_8	C_4H_{10}	CO	CO_2	$CO + CO_2$ (moles % on original cresol)
o-Cresol	71,6	22,4	1,35	0,7	0,25	1,3	0,4	4,2
m-Cresol	74,1	19,4	1,35	0,75	0,35	1,5	0,2	4,2
p-Cresol	68,8	23,5	2,0	0,8	0,5	2,0	0,4	6,0

* Methyl radicals are partially consumed in the alkylation of cresol; this fact, however, cannot have a substantial effect on the results of the calculation.

From the above approximate calculation it follows that the breakdown of the benzene nucleus of p-cresol under the conditions studied proceeds considerably more vigorously than that of o-cresol.

DISCUSSION OF EXPERIMENTAL RESULTS

In accordance with the views developed in communications from our laboratory [6, 7], the homogeneous destructive hydrogenation of aromatic hydrocarbons and their derivatives proceeds by a radical-chain mechanism with participation of molecular and atomic hydrogen. In the light of these views the results obtained in the present investigation on the homogeneous destructive hydrogenation of cresols are in accord with the following scheme (see also [8]):

$$OHC_6H_4CH_3 \longrightarrow OHC_6H_4\dot{C}H_2 + H^\cdot \tag{1a}$$

$$OHC_6H_4CH_3 \longrightarrow \dot{O}C_6H_4CH_3 + H^\cdot \tag{1b}$$

$$H^\cdot + OHC_6H_4CH_3 \longrightarrow C_6H_4CH_3 + H_2O \quad \text{or} \quad C_6H_5CH_3 + \dot{O}H \tag{2a}$$

$$H^\cdot + OHC_6H_4CH_3 \longrightarrow \dot{C}_6H_4OH + CH_4 \quad \text{or} \quad C_6H_5OH + \dot{C}H_3 \tag{2b}$$

$$H^\cdot + OHC_6H_4CH_3 \longrightarrow CO + \text{ hydrocarbon radicals} $$

$$\dot{R} + H_2 \longrightarrow RH + H^\cdot \tag{3}$$

$$\dot{C}H_3 + OHC_6H_4\dot{C}H_2 \longrightarrow OHC_6H_4C_2H_5 \tag{4}$$

$$\dot{C}H_3 + \dot{C}_6H_4OH \longrightarrow OHC_6H_4CH_3 \tag{5}$$

$$\dot{O}C_6H_4CH_3 + \dot{C}_6H_4CH_3 \longrightarrow (CH_3C_6H_4)_2O \tag{6}$$
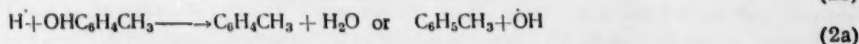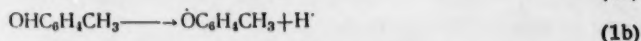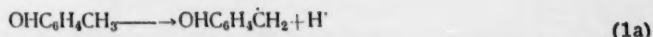
Reactions (1) are chain-initiation processes. However, the possibility cannot be excluded that reaction chains may be initiated also by the cleavage of OHC_6H_4-CH_3 bonds [9] (or $CH_3C_6H_4$-OH) and by the dissociation of molecular hydrogen [10]. Atomic hydrogen then reacts with cresol molecules by Reactions (2a), (2b), and (2c). The radicals R formed in Reactions (1) and (2) react with molecular hydrogen [Reaction (3)] with generation of atomic hydrogen. Reactions (4), (5), and (6) are chain-terminating processes which lead to the formation of ethylphenol, isomeric cresols, bistolyl ether, and other compounds.

At the same time there occurs further homogeneous destructive hydrogenation of toluene and phenol with formation of xylenols. The gaseous products undergo further transformations: carbon monoxide reacts with steam with formation of carbon dioxide; it is possible also that carbon monoxide reacts with hydrogen with formation of hydrocarbons (the over-all yield of gaseous products from the cleavage of the aromatic ring is greater than that calculated from their content of carbon monoxide and dioxide).

Our results (Table 3) indicate that homogeneous destructive hydrogenation proceeds most vigorously with o-cresol and least vigorously with m-cresol. Jones and Neuworth [8] found that the activation energy for the thermal decomposition of m-cresol is 6 kcal/mole greater than for o-cresol (the values are 75 and 69 kcal/mole, respectively). Hence, the results of our investigation confirm the view that there is a relation between homogeneous destructive hydrogenation and the thermal cleavage of the weakest bond in aromatic hydrocarbons and their derivatives.

Under the conditions studied demethylation and dehydroxylation of cresols are accompanied by cleavage of the aromatic rings of cresol and phenol, which is accelerated by increase in the pressure of hydrogen. The results of our investigation show that this reaction is least vigorous with o-cresol and proceeds 1.5-2 times as rapidly with p-cresol. m-Cresol, as far as can be judged from the results, reacts somewhat more slowly than p-cresol in this respect. Hence, the order found here differs from that found for the over-all rate of demethylation and dehydroxylation of the isomeric cresols.

We consider that the following is the probable explanation of the results. It is readily seen that the bond between a carbon atom carrying a hydroxy group and another carbon atom is weakened by the linkage of hydrogen to one of these two atoms:

                (I)   (II)
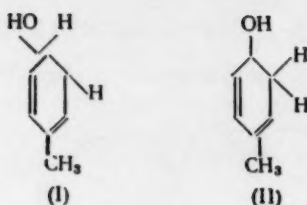
However, addition of atomic hydrogen with formation of the radical (I) in accordance with the scheme assumed previously [7] leads mainly to the dehydroxylation of cresol with formation of a tolyl radical and water (or toluene and the OH radical). Hence, it may be supposed that the cleavage of an aromatic ring with formation of carbon monoxide and C_1-C_4 (and also possibly C_5) hydrocarbons proceeds mainly as a result of the union of a hydrogen atom in the ortho position to the hydroxy group. The probability of such cleavage in o-cresol is approximately one-half of that of its occurrence in m- and p-cresols, because the tendency for the radical
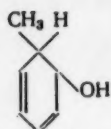
to undergo demethylation is very great.

The authors express their thanks to A. E. Gavrilova for valuable advice in the course of this investigation.

SUMMARY

1. An investigation was made of the homogeneous destructive hydrogenation of toluene, phenol, and o- m-, and p-cresols at 490° at initial hydrogen pressures of 100-300 atm.

2. Under these conditions the demethylation of toluene is almost twice as fast as the dehydroxylation of phenol.

3. By the homogeneous destructive hydrogenation of cresols yields of phenol of up to 30% by weight on the cresol can be attained.

4. With respect to the over-all rate of demethylation and dehydroxylation the cresols are in the order: o-cresol > p-cresol > m-cresol.

5. As well as demethylation and dehydroxylation, cresols, like phenol, undergo simultaneous cleavage of the aromatic ring. The tendency for cleavage to occur falls in the order: p-cresol > m-cresol > o-cresol.

6. The question of the mechanism of the cleavage of the aromatic ring in cresols was examined and a general radical-chain scheme for the homogeneous destructive hydrogenation of cresols was proposed; the scheme is confirmed by the results obtained on the compositions of the products of reaction-chain termination.

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SYNTHESIS OF ORGANOMERCURY NITRO COMPOUNDS

COMMUNICATION 1. MERCURATION OF AROMATIC AND HETEROCYCLIC COMPOUNDS
WITH THE MERCURY SALT OF TRINITROMETHANE

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Mercuration occupies a prominent place among methods for the preparation of aromatic organomercury compounds. The reaction conditions vary widely, depending on the structure of the aromatic compound, and as mercurating agents both mercuric oxide and its salts are used [1]. However, there are no reports in the literature of attempts to use the mercury salts of nitroalkanes as mercurating agents. It may be supposed that the mercury salts of aci-forms of nitroalkanes will tend to enter into a mercuration reaction in accordance with the general scheme:

$$ArH + HgX_2 \rightleftarrows ArHgX + HX.$$

We began this work with an investigation of the mercurating power of the mercury salt of trinitromethane, as a substance in which the tautomeric change into the aci-form occurs particularly readily. The mercury salt of trinitromethane was first prepared by Ley and Kissel [2] by the action of trinitromethane in ethereal solution on freshly prepared mercuric oxide:

$$2 CH(NO_2)_3 + HgO \rightarrow [C(NO_2)_3]_2 Hg + H_2O.$$

References to this substance in the literature are concerned mainly with its ability to exist in two mutually convertible forms [2-4].:

$$(NO_2)_3 C^{Hg/2} \rightleftarrows (NO_2)_2 C{=}NO_2^{Hg/2}.$$
$$(I) \qquad\qquad (II)$$
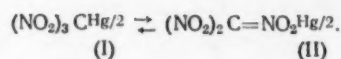
In the crystalline state, and also in nonpolar solvents, the mercury salt of trinitromethane is an organometallic compound (I). In alcohol this organometallic form is in equilibrium with the isomeric form (II), which is a derivative of the aci-form of trinitromethane. In very dilute aqueous solution the mercury salt passes completely into the derivative of the aci-form.

In connection with our investigation of the possibility of using the mercury salt of trinitromethane in the mercuration reaction, we decided to make a more detailed study of its physical and chemical properties. We found that the mercury salt of trinitromethane can be prepared by reaction between trinitromethane and mercuric oxide not only in ether, but also in water and in alcohol. The freshly prepared mercury salt decomposes, without melting, at 200-205°. When kept in the dry state or in ethereal solution the salt undergoes partial decomposition. Alcoholic and aqueous solutions are more stable, and in this form the mercury salt can be preserved

for several months. When heated in dibutyl ether it undergoes decomposition, which is particularly marked above 100°. The decomposition results in the formation of a precipitate, which is insoluble in organic solvents, water, and dilute mineral acids; it decomposes with an explosion and the liberation of metallic mercury at 145-150°. When treated with dilute aqueous potassium hydroxide, ammonia, or potassium iodide, the precipitate gives qualitative reactions characteristic of mercurous salts.

Treatment of the mercury salt of trinitromethane with potassium hydroxide results in the formation of the potassium salt of trinitromethane and mercuric oxide:

$$Hg\,[C\,(NO_2)_3]_2 + 2\,KOH \rightarrow 2\,KC\,(NO_2)_3 + HgO + H_2O.$$
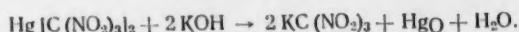
The mercury salt of trinitromethane is decomposed only very slowly (standing for two weeks) by potassium iodide; reaction occurs in accordance with the equation:

$$Hg\,[C\,(NO_2)_3]_2 + 2\,KI \rightarrow 2\,KC\,(NO_2)_3 + HgI_2.$$
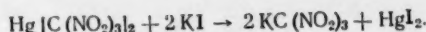
In the present work we studied the action of the mercury salt of trinitromethane on compounds of the aromatic and heterocyclic series: benzene, toluene, anisole, aniline, N,N-dimethylaniline, furan, thiophene, pyrrole, and 1-methylpyrrole. It was found that in the mercuration of these compounds (with the exception of the pyrroles) with the mercury salt of trinitromethane monomercurated derivatives were formed in yields of 30-70%:

$$RH + Hg\,[C\,(NO_2)_3]_2 \rightleftarrows RHgC\,(NO_2)_3 + HC\,(NO_2)_3.$$
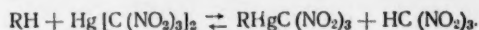
The mercuration of benzene and toluene was carried out in excess of these reagents at 80° for 3-5 hours; that of anisole, aniline, and N,N-dimethylaniline was carried out in alcohol at room temperature (80° in the case of anisole); and that of furan and thiophene — in moist ether at room temperature. In the mercuration of anisole and toluene the o- and p-isomers were isolated.

In aqueous and alcoholic solutions the mercury salt of trinitromethane does not react with benzene. The probable explanation is that, in these solvents, the mercury salt is in equilibrium not only with its aci-form, but also with its alkoxide [5]:

$$Hg\,[C\,(NO_2)_3]_2 + ROH \rightleftarrows ROHgC\,(NO_2)_3 + HC\,(NO_2)_3.$$
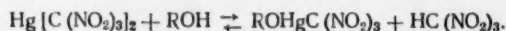
The free trinitromethane formed, being a strong acid ($K = 1.38 \cdot 10^{-2}$) [6], makes the mercuration of benzene, which is known to require severe conditions [1], still more difficult. On the other hand, the appearance of a feeble yellow color when the mercury salt of trinitromethane is dissolved in moist benzene* indicates the formation of the aci-form of the mercury salt, which is the mercurating agent.

In the reaction of the mercury salt of trinitromethane with aniline, N,N-dimethylaniline, and anisole in alcoholic solutions, the presence of free trinitromethane did not hinder the mercuration of these compounds, because amino and hydroxy derivatives of benzene readily react with mercury salts [1]. Much resinification occurred in the mercuration of furan and thiophene with the mercury salt of trinitromethane in aqueous or alcoholic solutions, and the yield of product did not exceed 5-10%; when the reaction was carried out in moist ether, the yield of monomercurated compound reached about 30%.

It is noteworthy that, in the mercuration of aniline with the mercury salt of trinitromethane, hydrogen of the amino group was replaced by mercury

$$C_6H_5NH_2 + Hg\,[C\,(NO_2)_3]_2 \rightarrow C_6H_5NHHgC\,(NO_2)_3 + HC\,(NO_2)_3.$$

whereas mercuric acetate mercurates aniline in the nucleus [7]. In the case of N,N-dimethylaniline the reaction product was N,N-dimethyl-p-(trinitromethylmercuri)aniline.
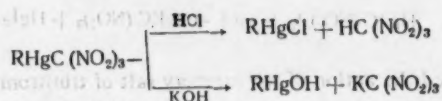
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*Moist benzene was used in the reaction.

After removal of solvent the mercuration products were carefully washed with water to remove unchanged mercury salt of trinitromethane and free trinitromethane liberated during the reaction. It is interesting that the formation of polymercurated compounds was not observed under our conditions. The monomercurated compounds obtained were readily soluble in alcohol (apart from the derivatives of aniline and N,N-dimethylaniline), acetone, and ether, but were insoluble in water: almost all of them melted with decomposition.

When treated with bromine in chloroform solution, aryl(trinitromethyl)mercurys give the corresponding arylmercury bromides and bromotrinitromethane:

$$RHgC (NO_2)_3 + Br_2 \rightarrow RHgBr + BrC (NO_2)_3$$

Concentrated hydrochloric acid converts them into arylmercury chloride, and caustic alkali converts them into the corresponding hydroxides:

$$RHgC (NO_2)_3 \begin{cases} \xrightarrow{\text{HCl}} RHgCl + HC (NO_2)_3 \\ \xrightarrow[\text{KOH}]{} RHgOH + KC (NO_2)_3 \end{cases}$$

The structures of the organomercury compounds synthesized were proved by replacement of the trinitromethyl group by halogen by reaction with potassium halide:

$$RHgC (NO_2)_3 + KX \rightarrow RHgX + KC (NO_2)_3$$

The ultraviolet spectra of the compounds synthesized were determined in polar and in nonpolar solvents with markedly different results; they were identical with the spectra obtained by Hantzsch for the mercury salt of trinitromethane in the respective solvents [3]. From this we may suppose that the mercuration products, like the mercury salt of trinitromethane, may exist, depending on the nature of the solvent, in two mutually convertible forms

$$RHgC (NO_2)_3 \rightleftarrows RHgO - N = C (NO_2)_2 \atop {\downarrow \atop O}$$
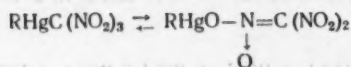
and are true organometallic compounds $RHgC(NO_2)_3$ in the crystalline state.

The mercuration of pyrrole and 1-methylpyrrole with the mercury salt of trinitromethane was carried out in ether or alcohol at −10°. The reaction products, which were insoluble in all solvents, decomposed without melting when heated. It is known that the action of mercuric chloride on pyrrole and its homologs results in the formation of insoluble substances of structure $(pyrrole)_2 Hg(HgCl_2)_4$ [8]. It is probable that, in our case also, reaction proceeds in the same direction.

EXPERIMENTAL

Preparation of the Mercury Salt of Trinitromethane

$$2 CH (NO_2)_3 + HgO \rightarrow (NO_2)_3 CHgC (NO_2)_3 + H_2O$$
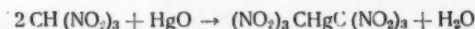
An ethereal solution (1:1 by volume) of 20 g (0.13 mole) of trinitromethane was added in small portions at room temperature to 16 g (0.07 mole) of freshly prepared mercuric oxide in 50 ml of ether;* the temperature rose to 30°. The reaction mixture was stirred for 15 minutes, and the ethereal solution was then filtered from the unchanged mercuric oxide. The ether was evaporated off, and the mercury salt of trinitromethane separated as a thick light-yellow oil, which crystallized in the course of 5-6 hours. The crystals were separated from the oil on a porous filter; decomposition temperature 200-205°; yield 26.5 g (80%). The mercury salt of

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*The mercury salt of trinitromethane can be prepared in quantitative yields in aqueous or alcoholic solutions.

trinitromethane is readily soluble in water, alcohol, chloroform, acetone, benzene, ether, ethyl acetate, and acetic acid; it is insoluble in petroleum ether, hexane, and isooctane.

Reaction of the Mercury Salt of Trinitromethane with Benzene
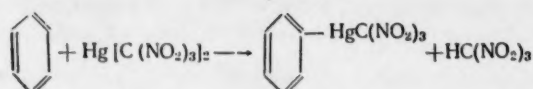
The mercury salt of trinitromethane (5 g) was dissolved in 20 ml of benzene and 3 ml of ether.* The solution was filtered from a small amount (50-100 mg) of inorganic impurity (decomposition products from the mercury salt) and heated for five hours in a water bath at 85-90°. The hot solution was then filtered; on cooling, colorless crystals of phenyl(trinitromethyl)mercury separated; they were filtered off and washed several times with water. Benzene was distilled from the mother liquor at 250 mm to give a residue of 5-10 ml, from which a further 0.5 g of phenyl(trinitromethyl)mercury was isolated. The total yield was 2.5 g (58.5%). Recrystallization from carbon tetrachloride gave 2 g of phenyl(trinitromethyl)mercury, m. p. 146°. Found: C 19.96; 19.90; H 1.33; 1.30; N 9.71; 9.71%. $C_7H_5N_3O_6Hg$. Calculated: C 19.70; H 1.18; N 9.85%.

To prove the structure of the phenyl(trinitromethyl)mercury that we prepared the following reactions were carried out.

Reaction of phenyl(trinitromethyl)mercury with potassium iodide.

$$C_6H_5HgC(NO_2)_3 + KI \longrightarrow C_6H_5HgI + KC(NO_2)_3$$

A hot solution of 0.4 g of KI in 5 ml of acetone was added to a solution of 1 g of $C_6H_5HgC(NO_2)_3$ in 5 ml of acetone; silvery crystals of phenylmercury iodide were precipitated immediately. They were filtered off and recrystallized from benzene; m. p. 265°. The literature [9] gives m. p. 266°.

### Reaction of phenyl(trinitromethyl)mercury with bromine.

$$C_6H_5HgC(NO_2)_3 + Br_2 \longrightarrow C_6H_5HgBr + BrC(NO_2)_3$$

A chloroform solution of bromine was added slowly at room temperature to a solution of 3 g of $C_6H_5Hg(NO_2)_3$ in 15 ml of chloroform until the bromine color persisted. As bromine was added a precipitate of phenylmercury bromide formed; it was filterd off and recrystallized from a 1:1 mixture of alcohol and benzene; m. p. 275°. The literature [10] gives m. p. 275°. Bromotrinitromethane was isolated from the chloroform solution; b. p. 69° (20 mm); $n^{20}D$ 1.4899. The literature [11] gives: b. p. 68° (20 mm); $n^{20}D$ 1.4900.

Reaction of phenyl(trinitromethyl)mercury with concentrated hydrochloric acid.

$$C_6H_5HgC(NO_2)_3 + HCl \longrightarrow C_6H_5HgCl + HC(NO_2)_3$$

A mixture of 1 g of $C_6H_5HgC(NO_2)_3$ and 10 ml of concentrated hydrochloric acid was heated for five minutes. A precipitate of phenylmercury chloride formed, and was filtered off, washed with water, and recrystallized from alcohol; m. p. 252°. The literature [12] gives m. p. 252°.

Reaction of the Mercury Salt of Trinitromethane with Toluene
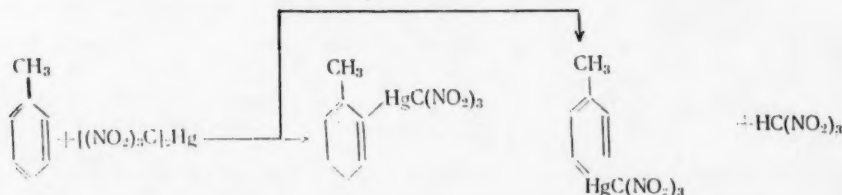
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*Ether was taken because of the high solubility of the mercury salt of trinitromethane in this solvent.

The mercuration of toluene was carried out under the same conditions as the mercuration of benzene. The reaction mixture was heated for three hours; it was then filtered, and the excess of toluene was distilled off at 10 mm to leave a residue of about 5 ml. The crystals of p-tolyl(trinitromethyl)mercury that separated were filtered off, washed with water, dried in air, and recrystallized from carbon tetrachloride; m. p. 149°. Found: C 21.45; 21.77; H 1.70; 1.73; N 9.49; 9.59%. $C_8H_7O_6N_3Hg$. Calculated: C 21.75; H 1.59; N 9.51%.

After addition of water, colorless crystals of o-tolyl(trinitromethyl)mercury separated; m. p. 126°. Total yield 51.5%. Found: C 21.98; 21.94; H 1.79; 1.76; N 9.65; 9.79%. $C_8H_7O_6N_3Hg$. Calculated: C 21.75; H 1.59; N 9.51%.

Reaction of o- and p-tolyl(trinitromethyl)mercury with potassium chloride.

$$o(p)\text{-}CH_3C_6H_4HgC(NO_2)_3 + KCl \longrightarrow o(p)\text{-}CH_3C_6H_4HgCl + KC(NO_2)_3$$

When an alcoholic solution of $p\text{-}CH_3C_6H_4HgC(NO_2)_3$ was treated with an equimolecular amount of KCl, crystals of p-tolylmercury chloride were precipitated. Their melting point after recrystallization from alcohol was 238°. The literature [13] gives m. p. 238–239°. On treatment of an alcoholic solution of $o\text{-}CH_3C_6H_4HgC(NO_2)_3$ with KCl no precipitate was formed, because o-tolylmercury chloride is readily soluble in alcohol. After removal of solvent o-tolylmercury chloride separated and was recrystallized from 50% alcohol; m. p. 145–146°. The literature [14] gives 145–146°.

Reaction of the Mercury Salt of Trinitromethane with Anisole

$$C_6H_5OCH_3 + Hg[C(NO_2)_3]_2 \longrightarrow o(p)\text{-}CH_3OC_6H_4HgC(NO_2)_3 + HC(NO_2)_3.$$
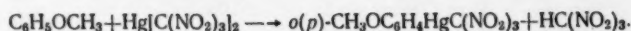
Anisole (2 ml) was mixed with 5 g of the mercury salt of trinitromethane in 7 ml of alcohol, and the mixture was heated at the boil in a water bath for 30 minutes. After removal of alcohol there remained a light-yellow oil which crystallized out completely after 2–3 hours. The crystals were washed with water and dried in air. The reaction gave a mixture of o- and p-methoxyphenyl(trinitromethyl)mercury. The isomers were separated by crystallization from 50% alcohol, in which the p-isomer is readily soluble. After recrystallization from carbon tetrachloride, o-methoxyphenyl(trinitromethyl)mercury had m. p. 114° (decomp.), and after crystallization from the same solvent p-methoxyphenyl(trinitromethyl)mercury had m. p. 101° (decomp.). Over-all yield 41%. Found: C 20.68; 20.69; H 1.36; 1.46; N 8.72; 8.83%. $C_8H_7O_7N_3Hg$. Calculated: C 20.99; H 1.69; N 9.18%.

Reaction of o- and p-methoxyphenyl(trinitromethyl)mercury with potassium chloride.

$$o\text{-}(p)\text{-}CH_3OC_6H_4HgCl + KC(NO_2)_3$$
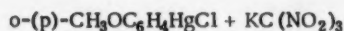
The reaction of o- and $p\text{-}CH_3OC_6H_4HgC(NO_2)_3$ with KCl was carried out under the same conditions as the reaction of the corresponding toluene derivatives. In the case of the para derivative the chloride obtained had m. p. 239° (from alcohol); the ortho chloride had m. p. 174–175° (from 50% alcohol). The literature gives m. p. 239° for p-methoxyphenylmercury chloride [15] and m. p. 174–175° for o-methoxyphenylmercury chloride [16].

Reaction of the Mercury Salt of Trinitromethane with Aniline

$$\langle\text{—}\rangle\text{—}NH_2 + Hg[C(NO_2)_3]_2 \longrightarrow \langle\text{—}\rangle NHHgC(NO_2)_3 + HC(NO_2)_3$$
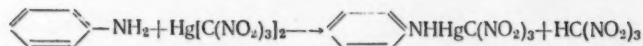
A solution of 5 g (0.01 mole) of the mercury salt of trinitromethane in 15 ml alcohol was added to an aniline solution of 2.5 g (0.027 mole) in 10 ml of alcohol. There was an immediate yellow precipitate, which was filtered off and washed with water, alcohol, and ether (alcohol was used for the removal of the aniline salt of trinitromethane*). When heated, the reaction product decomposed at 117° without melting; yield 2.6 g (59%). Found: C 18.96; 19.00; H 1.67; 1.76%. $C_7H_6O_6N_4Hg$. Calculated: C 18.98; H 1.36%.

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* The aniline salt of trinitromethane, which is not described in the literature, is readily prepared by reaction between equimolecular amounts of trinitromethane and aniline in ether. The salt is a yellow crystalline substance, insoluble in ether and cold water, but readily soluble in alcohol; at 130° it undergoes very vigorous decomposition.

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<u>Reaction of N-(trinitromethylmercuri)aniline with potassium chloride.</u>

$$C_6H_5NHHgC(NO_2)_3 + KCl \longrightarrow C_6H_3NHHgCl + KC(NO_2)_3$$

An alcoholic solution of 0.06 g of KCl was added to a boiling mixture of 0.3 g of $C_6H_5NHHgC(NO_2)_3$ in 25 ml of alcohol. Heating was continued further for 30 minutes, in the course of which a white powdery precipitate formed. The product was identical in properties with the N-(chloromercuri)aniline described in the literature [17].

Reaction of the Mercury Salt of Trinitromethane with N,N-Dimethylaniline
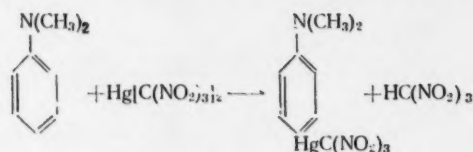

A solution of 4.8 g of N,N-dimethylaniline in an equal amount of alcohol was added to a solution of 5 g of the mercury salt of trinitromethane in 15 ml of alcohol. There was an immediate yellow precipitate, which was filtered off and carefully washed with alcohol to remove the dimethylaniline salt of trinitromethane. The reaction product, N,N-dimethyl-p-(trinitromethylmercuri)aniline, is insoluble in water, alcohol, and ether; it is readily soluble in acetone. The substance was purified by precipitation from acetone solution with water; it decomposed at 110° without melting. The mercuration product is not stable to storage.

<u>Reaction of N,N-dimethyl-p-(trinitromethylmercuri)aniline with potassium chloride.</u>

$$(CH_3)_2N\langle\!\!\langle\ \rangle\!\!\rangle HgC(NO_2)_3 + KCl \longrightarrow (CH_3)_2N\langle\!\!\langle\ \rangle\!\!\rangle HgCl + KC(NO_2)_3.$$

When 0.4 g of N,N-dimethyl-p-(trinitromethylmercuri)aniline in 10 ml of acetone was treated with an aqueous solution of potassium chloride (0.07 g), there was a precipitate of white crystals of p-(chloromercuri)-N,N-dimethylaniline, which was recrystallized from chloroform: m. p. 223-225° (decomp.). The literature [15] gives m. p. 225° (decomp.).

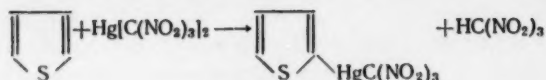### Reaction of the Mercury Salt of Trinitromethane with Furan
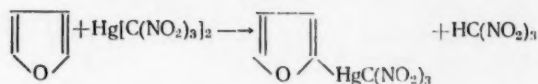
To an ethereal solution of 5 g of the mercury salt of trinitromethane we added 3.7 g (a sixfold excess) of freshly distilled furan. After 30 minutes the reaction mixture, which had a reddish color, was poured into 30 ml of water. After evaporation of the ether and excess of furan, furyl(trinitromethyl)mercury separated as a thick oil, which rapidly crystallized out. The crystals were washed with water, dried in air, and recrystallized from carbon tetrachloride; decomposition temperature 120°; yield 25%. Found: C 14.79; 14.71; H 0.85; 1.00; N 9.98; 10.03%. $C_5H_3O_7N_3Hg$. Calculated: C 14.38; H 0.76; N 10.01%.

<u>Reaction of furyl(trinitromethyl)mercury with potassium chloride.</u>

$$C_4H_3OHgC(NO_2)_3 + KCl \longrightarrow C_4H_3OHgCl + KC(NO_2)_3$$

A hot alcoholic solution of KCl was added to an equimolecular amount of $C_4H_3OHgC(NO_2)_3$ in alcohol. There was an immediate crystalline precipitate of 2-furylmercury chloride, which had m. p. 151° after recrystallization from alcohol. The literature [18] gives m. p. 151°.

Reaction of the Mercury Salt of Trinitromethane with Thiophene

$$\text{(thiophene)} + \text{Hg}[\text{C}(\text{NO}_2)_3]_2 \longrightarrow \text{(thiophene-HgC(NO}_2)_3) + \text{HC}(\text{NO}_2)_3$$

The mercuration of thiophene with the mercury salt of trinitromethane was carried out in the same way as the mercuration of furan. After recrystallization from carbon tetrachloride, thionyl(trinitromethyl)mercury had a decomposition temperature of 115°; yield 28%. Found: N 9.75; 9.87%. $C_5H_3O_6N_3HgS$. Calculated: N 9.68%.

Reactions of the Mercury Salt of Trinitromethane with Pyrrole and with 1-Methyl-pyrrole

The reaction between equimolecular amounts of the mercury salt of trinitromethane and pyrrole (or 1-methylpyrrole) in alcohol at −10° led to the formation of a yellow precipitate, which had to be removed rapidly from the trinitromethane-containing reaction mixture because the reaction product is resinified under the action of acids. The product decomposes at 122° (117° in the case of 1-methylpyrrole), and it is insoluble in water and in organic solvents. Both compounds give Ehrlich's reaction.

SUMMARY

1. The mercury salt of trinitromethane is a new mercurating agent for compounds of the aromatic and heterocyclic series.

2. Aromatic and heterocyclic compounds are mercurated with the mercury salt of trinitromethane with greater ease than with other mercury salts.

3. Aryl(trinitromethyl)mercurys can exist in two tautomeric forms:

$$\text{ArHgC}(\text{NO}_3)_2 \rightleftarrows \text{A rHgO}-\text{N}=\text{C}(\text{NO}_2)_2$$
$$\downarrow$$
$$\text{O}$$
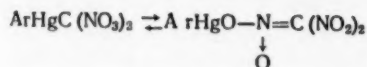
in the crystalline state they are true organometallic compounds.

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CATALYTIC POLYMERIZATION OF OLEFINS

COMMUNICATION 6. EFFECT OF ADDITIONS OF CERTAIN METAL OXIDES ON THE ACTIVITY OF A NiO—Al₂O₃—SILICA GEL CATALYST IN THE POLYMERIZATION OF ETHYLENE

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No. 3, pp. 513-518, March, 1960
Original article submitted July 21, 1958

It was shown in the preceding communication [1] that an addition of alumina has an activating effect on an NiO-silica gel (KSK) catalyst in the polymerization of ethylene at 300° and atmospheric pressure. In the present paper we present data obtained in a study of the effect of additions of certain metal oxides on the activity of an NiO-Al₂O₃-silica gel (KSK) catalyst in the same reaction. The effects of additions of Cu, Ag, Mg, Zn, Ca, Ba, Th, and Mn oxides were investigated; the oxides were introduced by treating the silica gel with an aqueous solution of the corresponding nitrate at the boil. In other respects the preparation of an impregnated catalyst from nickel formate was carried out as before [1]. Thus, the silica gel was given three treatments with solutions of nitrates, and after each treatment the nitrate ion was removed and the silica gel was dried at 120°. The treatments of the silica gel were usually carried out in the following order: first with a solution of the salt corresponding to the metal oxide to be added, then with the aluminum salt, and finally with the nickel salt.

Experiments on the polymerization of ethylene each ran for five hours at 300°, and the time of contact with the catalyst was 5-6 seconds. The catalyst layer was 5-7 cm in length. The apparatus and experimental procedure were as before [2].

The results are given in Tables 1 and 2. For comparison, in Table 3 we give the results of experiments with catalysts containing no additions of metal oxides other than Al₂O₃.

EXPERIMENTAL

Cupric oxide. Catalysts 188 and 199 (Table 1) were investigated; in the preparation of the former,treatment of the silica gel with aluminum nitrate preceded treatment with cupric nitrate solution. Catalyst 188 corresponded to the copper-free catalyst 184 (Table 3), and catalyst 199 corresponded to catalyst 169 (Table 3). The results show that addition of cupric oxide to an NiO-Al₂O₃-silica gel catalyst, while scarcely lowering the general activity of the catalyst, considerably increases its selectivity, which is indicated by the increase in the yield of ethylene dimer from 60-70% to 70-80% on the ethylene that reacted. However, the ease with which the catalyst is regenerated is somewhat less.

Silver oxide. Comparison of the actions of catalysts 182 (Table 1) and 174 (Table 3) shows that addition of silver oxide lowers the activity and stability of the catalyst and makes it incapable of regeneration by heat treatment in a stream of air; however, it raises the selectivity of the catalyst.

Magnesium oxide. Study of the data on the work of catalysts 221 and 222 (the same preparation) (Table 1) in comparison with data on catalyst 195 (Table 3) showed that the addition of magnesium oxide leads to a sharp

TABLE 1

Catalyst	Concn. of soln. of nitrate of added metal	Expt.	Amount of ethylene that reacts (%)	Yield of butene (% on ethylene passed)	Yield of butene (% on ethylene that reacts)	Yield of butene (g/liter of catalyzate per hr)	Yield of higher hydrocarbons (%) on ethylene passed	Yield of higher hydrocarbons (%) on ethylene that reacts
188*	Saturated Cu(NO₃)₂ solution	1—3	41,4—22,3	29,5—15,3	71,2—68,4	260—120	5,3—2,6	13,0—11,6
188	"	4**—5	20,8—7,3	16,1—3,6	66,6—50,0	120—40	1,9—0,7	9,3—9,3
199	"	1—3	35,3—15,2	28,4—9,7	80,5—63,6	227—75	4,4—1,8	13,8—11,8
199	"	4**	13,8	11,9	81,5	90	0,7	5,2
182*	0,1% AgNO₃ solution	1—2	33,7—11,2	26,0—9,0	77,0—80,0	212—76	4,8—1,3	14,2—11,2
182	"	3	0,0	0,0	0,0	0	0,0	0,0
221	0,1% Mg(NO₃)₂ solution	1—2	31,8—19,3	23,6—11,6	74,2—60,6	230—100	4,3—2,0	13,4—10,0
221	"	3**	13,3	6,0	45,0	45	1,5	11,1
222	"	1—2	45,0—23,5	34,0—16,4	75,5—70,0	257—125	4,4—2,5	9,8—11,6
222	"	3	2,7	0,0	0,0	0	0,0	0,0
222	"	4**	9,9	0,0	0,0	0	0	0
194	0,1% Zn(NO₃)₂ solution	1—2	37,2—10,7	28,4—8,0	76,2—80,0	280—95	3,6—1,7	9,7—16,7
198	"	1—2	31,9—9,0	26,2—7,6	84,7—82,5	220—66	3,3—1,3	10,7—13,9
198	"	3**	19,2	18,5	78,2	121	3,1	16,2

* The first treatment of the silica gel was impregnation with aluminum nitrate solution.

** Before this experiment the catalyst was regenerated in a stream of air at 450° for five hours.

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TABLE 2

Catalyst	Concn. of soln. of nitrate of added metal	Expt.	Amount of ethylene that reacts (%)	Yield of butene			Yield of higher hydrocarbons (%)	
				(% on ethylene passed)	(% on ethylene that reacts)	(g/liter of catalyzate per hr)	on ethylene passed	on ethylene that reacts
218	0.1% Ca(NO₃)₂ solution	1—2	31,2—18,1	22,1—12,5	70,7—69,3	209—104	3,8—2,0	12,3—11,1
219	"	1—2	30,1—16,4	21,2—11,4	70,3—69,2	190—90	3,8—1,4	12,3— 8,7
219	"	3*	9,3	5,5	60,0	50	1,2	13,3
220	"	1—2	35,0—10,0	24,0— 7,7	68,0—77,0	182—63	5,1—1,7	14,6—16,7
220	"	3*	11,5	6,7	59,0	53	1,4	12,4
197	0.1% Ba(NO₃)₂ solution	1—2	24,9—5,3	19,4— 5,3	78,1—80,0	160—30	3,3—1,2	12,2—20,0
197	"	3*	7,6	6,5	78,5	47	1,4	18,6
185**	0.1% Th(NO₃)₄ solution	1	12,5	8,6	69,1	76	2,2	15,2
186	"	1—2	37,7—22,0	30,0—13,7	79,5—62,2	238—109	4,9—2,8	13,0—12,7
186	"	3*	19,5	14,3	73,5	121	2,6	13,5
187***	"	1—2	35,0—21,5	24,4—17,2	66,6—54,5	188—152	3,6—1,9	10,6— 8,8
189***	0.05% Th(NO₃)₄ solution	1—2	35,7—15,0	23,4—12,0	64,4—80,0	180—100	5,4—2,0	23,3—13,5
204	0.2% Mn(NO₃)₂ solution	1—4	31,6—17,9	29,9—14,6	79,0—81,5	217—118	3,8—2,1	12,2—11,5
204	"	5*	16,2	14,0	86,0	119	2,1	13,0
204	"	6*	9,9	7,2	73,0	62	1,3	13,0
205	"	1—3	40,0—21,0	25,2—15,3	63,0—73,0	207—118	4,4—2,9	11,0—13,7

* Before this experiment the catalyst was regenerated in a stream of air at 450° for five hours.

** In this catalyst Al₂O₃ was replaced by ThO₂.

*** Impregnation of the silica gel with aluminum nitrate solution formed the first treatment.

**** The impregnation of the silica gel with aluminum and thorium salts was carried out simultaneously with a solution of a mixture of the salts.

TABLE 3

| Catalyst | | Amount of ethylene that reacts (%) | Yield of butene | | | Yield of higher hydrocarbons (%) | |
No.	Expt.		(% of ethylene passed)	(% on ethylene that reacts)	(g/liter of catalyzate per hr)	on ethylene passed	on ethylene that reacts
184	1—2	50,3—24,7	30,7—17,6	61,1—71,4	220—150	6,6—4,0	13,2—15,8
184	3—4	19,2—19,0	14,9—11,8	77,4—62,0	110—90	3,5—2,4	17,4—15,5
184	5*	24,8	15,6	62,8	110	4,0	16,0
169	1—2	47,0—22,3	27,5—14,4	58,5—65,0	207—113	5,4—3,5	12,5—15,8
174	1—2	53,8—26,0	30,3—21,2	57,0—81,8	240—170	8,7—3,6	16,2—13,8
174	3*—4	26,7— 8,4	24,0— 6,6	90,0—79,0	177—51	3,0—2,1	11,2—25,5
195	1—2	53,0—33,5	33,3—22,7	63,0—67,7	280—200	10,2—5,3	19,7—16,0
195	3—4	28,3—20,3	17,6—11,2	62,2—55,1	140—80	4,5—2,3	16,2—11,6

* Before this experiment the catalyst was regenerated in a stream of air at 450° for five hours.

fall in the catalytic stability of an NiO-Al$_2$O$_3$-silica gel catalyst and to loss in its ability to be regenerated when heated in a stream of air. The selectivity of the catalyst rises somewhat before regeneration and falls sharply after its first treatment with air at 450°.

Zinc oxide. Comparison of the data on the work of catalysts 194 and 198 (Table 1) (which do not differ from one another in method of preparation), on the one hand, with the data on catalyst 184 (Table 3), on the other, showed that addition of zinc oxide to the carrier greatly increases the selectivity of an NiO-Al$_2$O$_3$-silica gel catalyst, while scarcely affecting its activity. Thus, whereas with catalyst 184, which did not contain zinc oxide, the yield of dimer was 30.7-17.6% on the amount of ethylene passed and 61.1-71.4% on the amount that reacted, with catalyst 194, which contained zinc oxide, the yield of dimer was 28.4-8.0% on the amount passed and 76.2-80.0% on the amount that reacted. A similar catalyst, catalyst 198, gave a yield of dimer of 84.7-82.5% on the ethylene that reacted, and it could be regenerated to a large extent with preservation of its selectivity. It is interesting that replacement of alumina by zinc oxide in an NiO-Al$_2$O$_3$-silica gel catalyst leads to complete loss of activity in the polymerization reaction.

Calcium oxide. Comparison of the work of catalysts 218, 219, and 220 (the same preparation; Table 2), on the one hand, with data for catalyst 195 (Table 3), on the other, shows that addition of calcium oxide to the carrier leads to a considerable fall in the activity and catalytic stability of the catalyst. The latter loses its ability to be regenerated when heated in a stream of air. The addition of calcium oxide also somewhat raises the selectivity for dimerization, but this selectivity disappears after treatment of the catalyst with air at 450°.

Barium oxide. Comparison of the work of catalyst 197 (Table 2) with that of catalyst 184 (Table 3) shows that the addition of barium oxide greatly lowers the activity and catalytic stability of an NiO-Al$_2$O$_3$-silica gel catalyst and deprives it of its ability to be regenerated when heated in air. The addition of barium oxide greatly increases the selectivity of the catalyst for the dimerization of ethylene.

Thorium dioxide. Comparison of catalysts 185, 186, 187, and 189 (Table 2), on the one hand, with catalyst 184 (Table 3), on the other, shows that thorium dioxide cannot replace alumina in an NiO-silica gel catalyst. The addition of thorium oxide to an NiO-Al$_2$O$_3$-silica gel catalyst has a slight deactivating effect, which is dependent on the order in which thorium and aluminum oxides are introduced into the catalyst.

Manganous oxide. Study of the work of catalysts 204 and 205 (the same preparation; Table 2) and of catalyst 184 (Table 3) showed that the addition of manganous oxide considerably raises the stability and selectivity of an NiO-Al$_2$O$_3$-silica gel catalyst with scarcely any change in activity, but it completely deprives the catalyst of its ability to be regenerated when heated in a stream of air.

From the results obtained in the investigation, in the previous work [1], of the activating effect of Al$_2$O$_3$ on an NiO-silica gel (KSK) catalyst and, in the present work, of various oxides on an NiO-Al$_2$O$_3$-silica gel

catalyst, a certain resemblance is seen in the behavior of silica gel, alumina (alumina gel), and systems composed of silica gel and alumina as catalysts for various reactions, on the one hand, and as carriers for NiO catalysts for the polymerization of ethylene, on the other. It is known that systems composed of silica gel and alumina gel (aluminosilicates) are catalytically active in cracking [3-5], polymerization [6-7], alkylation [8,9], isomerization [10], and other reactions, whereas silica gel and aluminum oxide (alumina gel), taken separately, have little or no activity. It has been shown in many cases that the activity of the aluminosilicate is due neither to change in specific surface nor to porosity [4, 11, 12], but to the appearance of a new phase, a hydrated aluminosilicate that is similar to montmorillonite and is formed from the components in the freshly prepared condition. The highest activity corresponds to the formation of $Al_2O_3 \cdot 4SiO_2$ [13].

The aluminosilicate carrier of an NiO polymerization catalyst can only be regarded as a carrier in a conventional sense, because its nature affects the activity of the catalyst in a very fundamental way. Correspondingly, hydrated aluminosilicate must be regarded as an active part of the catalyst side by side with nickel. In fact, aluminosilicates are active catalysts for the polymerization of butenes and propene [6, 7, 14]. However, ethylene is not polymerized in their presence, and only the introduction of nickel oxide will confer some activity for the polymerization of ethylene, though only to a small degree, i.e., mainly with respect to dimerization. It is known that a process promoted by aluminosilicates is a phenomenon of acid catalysis [6] in that, according to Vernadskii [15], these substances, unlike aluminum hydroxide $Al(OH)_3$ and silicic acid $Si(OH)_4$, are weak acids. Aluminum and silicon can replace one another in $(AlO_4)^{5-}$ and $(SiO_4)^{4-}$, which have the form of tetrahedra of oxygens with Al or Si in the center. The aluminum ion often has a coordination number of four, so that for every aluminum ion, which is attached to four oxygen atoms, to each of which one atom of silicon is attached, a hydrogen or equivalent metal ion is required to bring the system into a saturated state [16, 17]. This is in good agreement with the observations of various investigators on the deactivation of aluminosilicate catalysts on dehydration [18, 19] and on the addition of alkali [6, 20]. Deactivation with alkali or alkaline-earth metal cations amounts to the replacement of hydrogen ions by these metal cations. Organic bases have an analogous effect (e.g., pyridine and quinoline). On the other hand, in accord with this view aluminosilicates can be activated by treatment with acids.

The study of the effect of additions of oxides of various metals on the activity of a catalyst for the polymerization of ethylene showed that some additions, e.g., Ag, Ca, and Ba oxides, greatly reduce the activity, whereas others (Cu, Zn, Mn, Mg, and Th oxides) scarcely affect the activity. In this respect our results are in close accord with those of Bitepazh [20], who compared the catalytic activities of aluminosilicates impregnated in salt solutions for the cracking reaction. In these experiments the activity of the catalyst depended on the salt with which it was impregnated and fell in the following order: salts of Th, Al, Mg, Zn, and Ba.

SUMMARY

1. An investigation was made of the effect of additions of copper, silver, zinc, magnesium, calcium, barium, thorium, and manganese oxides on an $NiO-Al_2O_3$-silica gel (KSK) catalyst.

2. An addition of silver, calcium, or barium oxide greatly reduced the activity of the catalyst, but an addition of copper, zinc, manganese, or magnesium oxide had scarcely any effect on the activity. Thorium dioxide reduced the activity slightly.

3. An addition of copper, silver, zinc, barium, or manganese oxide considerably increased the selectivity of the catalyst for the dimerization of ethylene. This effect was shown to less extent by additions of magnesium and calcium oxides.

4. The catalytic stability of the catalyst was greatly lowered by an addition of magnesium or barium oxide and appreciably lowered by an addition of silver or calcium oxide. The stability was raised by addition of manganese oxide.

5. The regenerability of a catalyst is lowered by addition of copper or zinc oxide and disappears completely when silver, magnesium, calcium, or barium oxide is present in the catalyst. When the catalyst is treated with air at 450°, its selectivity is lost when it has an addition of silver, magnesium, or calcium oxide and is preserved when it has an addition of manganese oxide.

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CATALYTIC DISPROPORTIONATION OF
ALKYL(AND ALKENYL)DICHLOROSILANES

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Alkyl(and alkenyl)dichlorosilanes are widely used in addition reactions with various unsaturated compounds [1-5]

$$\equiv SiH + HR'C = CR''H \rightarrow \; \equiv SiCR'H{-}CR'H_2,$$
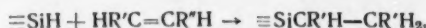
and in reactions in which the silicon-attached hydrogen is replaced by a group [6-8]

$$\equiv SiH + RX \rightarrow \; \equiv SiR + HX$$

(in which RX is,e.g., CH_4, C_2H_6, $CH_2 = CHCl$, C_6H_6, and $CH_3C_6H_5$). It would, of course, be interesting to study the use of alkyl(or alkenyl)monochlorosilanes, i.e., compounds of the type $RSiClH_2$, in these and other reactions. However, the synthesis of $RSiClH_2$, particularly by the disproportionation of the readily available $RSiCl_2H$, has as yet received very little investigation. In a recent investigation by Dolgov, Voronkov, and Borisov [9] it was shown for the first time that compounds of the type $RSiClH_2$ ($R = CH_3$ or C_2H_5) can be prepared by the disproportionation of the corresponding alkyldichlorosilanes with the aid of $AlCl_3$. There are also references in patents [10, 11] to the possibility of similar disproportionation with the aid of certain nitrogen-containing compounds, in particular dinitriles.

The present investigation was concerned with the disproportionation of alkyl(and alkenyl)dichlorosilanes with the object of obtaining alkyl(and alkenyl)monochlorosilanes. After tests on several possible catalysts, including phthalonitrile, quinoline, and triethylamine, without satisfactory results, we concentrated our attention on the investigation of adiponitrile and pyridine as catalysts (there was no reference in the literature to the possible use of the latter as a catalyst for the disproportionation reaction). The reaction invariably proceeded in accordance with scheme (1)

$$2\,RSiCl_2H \rightarrow RSiClH_2 + RSiCl_3,$$
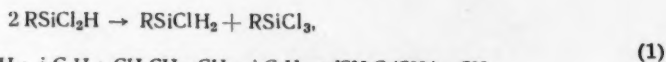
where $R = C_2H_5$; $n\text{-}C_3H_7$; $i\text{-}C_3H_7$; $CH_2CH = CH_2$; $i\text{-}C_4H_9$ and $CH_2C(CH_3) = CH_2$, (1)

and no products of further disproportionation formed by the possible scheme (2)

$$2\,RSiClH_2 \rightarrow RSiCl_2H + RSiH_3, \qquad (2)$$
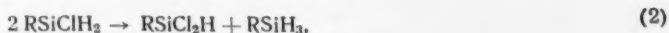
were formed.

The results of experiments on the yields of compounds of type $RSiClH_2$ with different catalysts and with different original amounts of $RSiCl_2H$ are presented in Table 1 and in Figs. 1-6. The properties of alkyl(and-alkenyl)chlorosilanes synthesized for the first time are given in Table 2. Pyridine was found to be similar to adiponitrile in its catalytic action on allyldichlorosilane, but was the more effective with dichloroethylsilane (experiments 5, 10, and 11, Table 1).

It was shown that considerable amounts of catalyst were necessary to give maximum disproportionation. Thus, in experiments 1-4 (Table 1) it was found that the optimum amount of adiponitrile for the disproportionation of allyldichlorosilane is 60-70 moles percent (the yields of $RSiClH_2$ and $RSiCl_3$ were 70-80% *), whereas if only about 2 moles percent of this catalyst was used the yields were only 10-12%. For 15 and 30 moles percent of adiponitrile the conversions were intermediate in value.
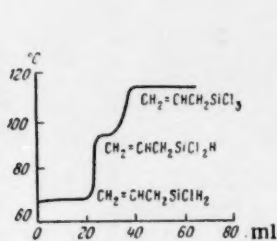
Fig. 1.
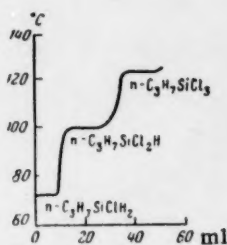
Fig. 2.
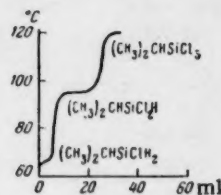
Fig. 3.
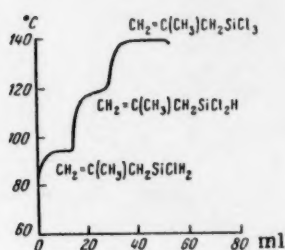
Fig. 4.
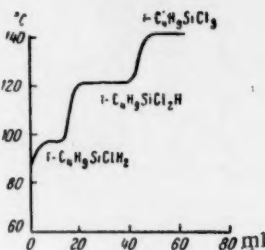
Fig. 5.
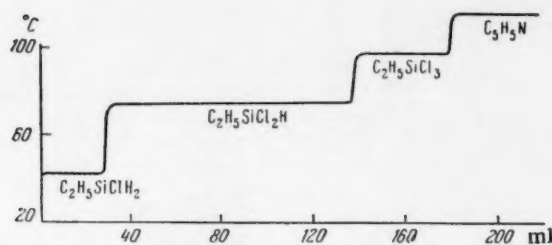
Fig. 6.

In the experiments with $CH_2=CHCH_2SiCl_2H$ the yields of allyltrichlorosilane were somewhat lower than those of allylchlorosilane; in all other cases the position was the reverse (see Table 1). The yields of $RSiClH_2$ and $RSiCl_3$ on the amount of $RSiCl_2H$ that reacted were 70-99%. Exceptions were experiments 1 and 11, in which the low yields of conversion products are clearly to be explained by the low amounts of products and

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* Calculated on the amount of $RSiCl_2H$ taken for reaction.

TABLE 1

Expt.	Starting substance	Wt. of reactant (g and moles)	Catalyst	Wt. of catalyst (g and moles)	Reaction time (hours)	Temp. in vapor of condensate* (°C)	Wt. of condensate (g)	Amt. of unchanged $RSiCl_2H$ (g and moles)	Yield of $RSiCl_2H_2$ (g and moles)	(% on $RSiCl_2H$ taken)	(% on $RSiCl_2H$ that reacted)	Yield of $RSiCl_3$ (g and moles)	(% on $RSiCl_2H$ taken)	(% on $RSiCl_2H$ that reacted)
1	Allyldichlorosilane CH_2=$CHCH_2SiCl_2H$	78,0 / 0,55	Adiponitrile	1,0 / 0,01	8,5	87—92	72	60,5 / 0,43	3 / 0,028	10	47	6 / 0,034	12	57
2	"	70,5 / 0,50	"	8,1 / 0,075	8,0	75—80	68,5	35,0 / 0,25	12,9 / 0,124	50	90	20,3 / 0,115	46	92
3	"	70,5 / 0,50	"	16,0 / 0,15	8,0	72—80	68,8	32,5 / 0,23	13,8 / 0,130	52	96	20,5 / 0,117	47	87
4	"	72,5 / 0,51	"	35,0 / 0,32	8,0	70—75	68,5	15,3 / 0,11	20,7 / 0,195	77	97	31,5 / 0,180	71	90
5	"	35,2 / 0,25	Pyridine	11,8 / 0,15	8,0	80—90	**	19,0 / 0,135	6,0 / 0,057	46	98			
6	Dichloropropylsilane $CH_3CH_2CH_2SiCl_2H$	55,0 / 0,38	Adiponitrile	27,0 / 0,25	6,5	81—88	51	25,9 / 0,18	8,5 / 0,079	42	79	16,8 / 0,095	50	95
7	Dichloroisopropylsilane $(CH_3)_2CHSiCl_2H$	40 / 0,28	"	20,0 / 0,185	10,0	85—90	26	15,8 / 0,11	2 / 0,019	13	22	7,9 / 0,045	32	53
8	Dichloro(2-methylallyl) CH_2=$(CH_3)CCH_2SiCl_2H$	51,0 / 0,33	"	25,0 / 0,24	5,0	93—98	48	12,3 / 0,08	9,6 / 0,080	49	64	23,5 / 0,124	75	99
9	Dichloroisobutylsilane $(CH_3)_2CHCH_2SiCl_2H$	74 / 0,47	"	30,0 / 0,28	5,25	98—108	70,3	26,8 / 0,17	11,1 / 0,09	38	60	27,3 / 0,142	60	95
10	Dichloroethylsilane $C_2H_5SiCl_2H$	210 / 1,63	Pyridine	90 / 1,14	35,5	65—70	**	119 / 0,92	85 / 0,26	32	71	47 / 0,29	36	82
11	"	85 / 0,66	"	20 / 0,25	5,25	65—70	**	58 / 0,45	3,2 / 0,034	10	32	5,2 / 0,032	10	30
12	"	200 / 1,55	Adiponitrile	96 / 0,89	7,5	70—73		170 / 1,32	6,6 / 0,07	4	61	13,5 / 0,08	5	69
13	Dichloromethylsilane CH_3SiCl_2H	68 / 0,59	"	39,5 / 0,36	8,5	40—41	Starting material all recovered unchanged							

* Temperature measured in the vapor of the condensate after one hour; this was maintained during the rest of the experiment.

** The weight of condensate could not be determined because of the closeness of the boiling points of the products to that of pyridine.

TABLE 2

Properties of Alkyl(and Alkenyl)chlorosilanes

Substance	Name and Formula of substance	B. p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR found	MR calculated	Found (%) C	H	Si	Cl	Calculated (%) C	H	Si	Cl
I*	Allylchlorosilane $CH_2=CHCH_2SiClH_2$	68,2 (745)	1,4290	0,9193	29,89	30,14	33,81 33,89	6,73 6,62	25,98 25,78	32,53 32,56	33,79	6,63	26,31	33,25
II°	Chloropropylsilane $CH_3CH_2CH_2SiClH_2$	73,0 (750)	1,4096	0,8901	30,21	30,43	33,29 32,98	8,36 8,37	25,85 25,52	32,08 32,19	33,16	8,35	25,82	32,63
III*	Chloroisopropylsilane $(CH_3)_2CHSiClH_2$	67—68 (740)	1,4040	0,8734	30,43	30,43			24,96 21,81	32,97 33,09			25,82	32,63
IV*	Chloro(2-methylallyl)silane $CH_2=(CH_3)CCH_2SiClH_2$	93,5—94,0 (746)	1,4381	0,9176	34,51	34,64	39,80 39,52	7,88 7,64	22,47 22,66	29,46 29,40	39,82	7,51	23,25	29,39
V*	Chloroisobutylsilane $(CH_3)_2CHCH_2SiClH_2$	96,5—97 (751)	1,4166	0,8935	34,49	34,98			21,33 21,00	28,50 28,73			22,87	28,90
VI***	Chloroethylsilane $C_2H_5SiClH_2$	42 (749)	1,3960	0,8887	25,57	25,68								

* Substance prepared for the first time.

** Calculated with the aid of the group refractions proposed by Mironov and Nikishin [17].

*** This substance, prepared by a different method [9], had the properties: b. p. 43° (751 mm); n_D^{20} 1,3975; d_4^{20} 0,9013; found MR 25,31, calculated MR 25,72.

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therefore relatively large losses. In Expt. 7 [with $(CH_3)_2CHSiCl_2H$] we observed much gas formation and the appearance of low-boiling liquids of unestablished composition; this did not occur in the other experiments.

In the course of our study of reaction (1) we found that the structure of the hydrocarbon group in $RSiCl_2H$ has a substantial effect on the reaction rate. Thus, in the disproportionation of $RSiCl_2H$, in which R is $(CH_3)_2CH$ (A), $CH_3CH_2CH_2$ (B), or $CH_2=CHCH_2$ (C), in presence of 60-70 moles percent of adiponitrile the conversion of $RSiCl_2H$ falls sharply in the order C > B > A (experiments 1, 6, and 7, Table 1).

From the fractionation curves obtained in these experiments (Figs. 1, 2, and 3) it is clearly seen that the relative amount of unchanged $RSiCl_2H$ increases in the order C < B < A. In the case of C the higher reaction rate was confirmed by the higher rate at which the temperature in the condensate vapor fell. It should be noted that the compounds of type $RSiCl_2H$ used have similar boiling points, so that their differing activities in this reaction cannot be explained by differing reaction temperatures.

Under analogous conditions, of the two structurally similar compounds

$$CH_2=(CH_3)CCH_2SiCl_2H \text{ and } CH_3-(CH_3)CHCH_2SiCl_2H$$
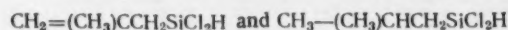
the latter compound again undergoes less active conversion (experiments 8 and 9, Table 1, and Figs. 4 and 5).

Table 1 shows that reduction of the size of the group R in $RSiCl_2H$ to that of ethyl (Expt. 12) results in greater retardation of reaction, and when R = CH_3 the reaction does not occur at all, even though the amount of catalyst taken (60-70 moles percent) is the same as in the case of the higher alkyldichlorosilanes. This reduction in the conversion with reduction in the size of the group is probably to be explained by the nature of the silicon-attached group and the specific action of the catalyst, rather than by simple reduction in reaction temperature. It is interesting that Dolgov, Voronkov, and Borisov [9], who carried out reaction (1) with $C_2H_5SiCl_2H$ and $n-C_4H_9SiCl_2H$ over $AlCl_3$, showed that the conversion was several times as high in the case of dichloroethylsilane as in the case of the higher-boiling $n-C_4H_9SiCl_2H$. The cause of these contradictory results probably lies in the different characters of the catalysts.

EXPERIMENTAL

The original alkyl(and alkenyl)dichlorosilanes were prepared by known methods [12-15] and carefully fractionated through columns having 20-30 theoretical plates; allyldichlorosilane, which according to the literature [12] has b. p. 97° and d_{27}^{27} 1.086, had the following properties as prepared by us: b. p. 95.2° (740 mm); n_D^{20} 1.4393; d_4^{20} 1.0931. The catalysts used were commercial adiponitrile, triethylamine, and other substances after careful drying and distilling. For shortness in description, the experimental results are given in Table 1. We here describe only two characteristic experiments.

Experiment 4. A mixture of 72.5 g of allyldichlorosilane and 35 g of adiponitrile was prepared in a still fitted with a column of 20-plate efficiency having a nichrome filling. The column communicated to the atmosphere through a receiver, which was connected with polyvinyl chloride tubing, followed by spiral trap at $-70°$ and a Tishchenko vessel containing toluene. The contents of the still were heated to the boil, when the two-layered liquid became homogeneous; for the first 30-40 minutes gas was liberated at the rate of one bubble every 1-2 seconds. At the end of this time the temperature had settled down at 69°, and gas evolution diminished sharply. Collection of condensate was then started at such a rate that the temperature of the condensate vapor did not vary outside the range 70-75°. After 7 hours 15 minutes the temperature had still not fallen below 75° with the tap open during 40 minutes of the work of the column, and the remaining reaction products were then distilled off rapidly at temperatures up to 119°. There was no appreciable amount of liquid in the trap. The weight of condensate was 66 g. Fractionation of the dark-colored residue in the still from a Claisen flask gave a further 2.5 g of allyltrichlorosilane (n_D^{20} 1.4453; d_4^{20} 1.2230) and 29.5 g of adiponitrile, b. p. 129-134° (3 mm). The residue (4.5 g) was a dark-colored resin which solidified when cool. The combined condensate was fractionated through the 20-plate column. We obtained $C_3H_5SiClH_2$ (see Table 1), $C_3H_5SiCl_2H$ (unchanged), and $C_3H_5SiCl_3$; b.p. 116.0-116.6°; n_D^{20} 1.4450; d_4^{20} 1.2226. The literature data for allyltrichlorosilane [12] is: b.p. 117.5°; d_{27}^{27} 1.211. The same substance specially prepared by us by the method in [12] and carefully fractionated through a column had the following properties: b.p. 116.5-116.7° (750 mm); n_D^{20} 1.4447; d_4^{20} 1.2224; the residue in the still (3.8 g) was colorless and had n_D^{20} 1.4460 and d_4^{20} 1.2231, i.e., was also $C_3H_5SiCl_3$. The fractionation curve is shown in Fig. 1.

Experiment 10. The reaction was carried out in an apparatus differing from that described in Expt. 4 in that the column with the nichrome filling was replaced by a Vigreux column 400 mm in length and 20 mm in diameter. For the reaction we took 210 g of dichloroethylsilane and 90 g of pyridine. A white precipitate formed when the reactants were mixed, but this partially redissolved at the boil. Heating was continued for 34 hours 30 minutes with four overnight interruptions. In the course of this time we collected 57 g of a fraction of b. p. 65-70°, after which the tap was opened and the remaining products were distilled off up to 116.5°. The residue (10 g) was a gray solid. About 15 ml of condensate of b. p. above room temperature collected in the trap. The 65-70° fraction and the condensate from the trap were combined and fractionated through the 20-plate column. After the separation of chloroethylsilane (see Table 2) the residue was combined with the 70-116.5° distillate and fractionation was continued with separation of $C_2H_5SiCl_2H$ and $C_2H_5SiCl_3$; b. p. 97-97.6° (740 mm); $n^{20}D$ 1.4258 and d^{20}_4 1.2415. In addition we isolated 78.9 g of unchanged pyridine, b. p. 114-116.2°. The fractionation curve is shown in Fig. 6.

Experiments 1-3, 5-9, and 10-13 were carried out similarly to Expts. 4 and 10. In the determination of yields of disproportionation products (Table 2) account was taken of intermediate fractions and of still residues from the second fractionation.

In Expt. 6 (Fig. 2) we obtained trichloropropylsilane; b. p. 121.5-123.5° (750 mm); $n^{20}D$ 1.4301; d^{20}_4 1.870. The literature [14] gives: b. p. 122.2° (740 mm); n^{20} 1.4290; d^{20}_4 1.1851. In Expt. 7 (Fig. 3) we obtained trichloroisopropylsilane; b. p. 118.5-121° (740 mm); $n^{20}D$ 1.4315. The literature [14] gives: b. p. 120.3° (748 mm); $n^{20}D$ 1.4319. In Expt. 8 (Fig. 4) we isolated trichloro(2-methylallyl)silane; b. p. 139.5° (746 mm); $n^{20}D$ 1.4540; d^{20}_4 1.1980. The literature [15] gives: b. p. 139° (743 mm); $n^{20}D$ 1.4533; d^{20}_4 1.1990. In Expt. 9 (Fig. 5) we obtained trichloroisobutylsilane; b. p. 140.5-143° (750 mm); $n^{20}D$ 1.4370. The literature [4] gives: b. p. 139.5° (745 mm); $n^{20}D$ 1.4358.

To investigate the structures of the compounds obtained we determined their Raman spectra.

Raman spectra ($\Delta\nu$ in cm^{-1}) *

$H_2ClSi-CH_2-CH_2-CH_3$: 148 (2 sh), 169 (0), 253 (1 b), 358 (2), 431 (1 b), 511 (8 b), 556 (1), 601 (0), 692 (3 b), 747, (2 b), 810 (1 b), 895 (1 b, db), 954 (4 b), 1016 (0), 1037 (3), 1075 (1), 1108 (1), 1206 (3), 1301 (1 b), 1351 (1 b), 1454 (4 b), 2181 (19 b), 2874 (10), 2911 (2), 2936 (4), 2967 (3).

$HCl_2Si-CH_2-CH_2-CH_3$: 150 (2), 174 (3), 186 (2), 209 (0), 244 (1), 273 (3), 295 (1 b), 351 (2), 401 (2), 455 (0 b), 498 (9 b), 515 (2), 556 (2 b), 568 (2 b), 649 (0 b), 690 (1 b), 719 (0 b), 747 (1 b), 809 (2 b), 846 (1 b), 884 (2 b. db) 979 (0), 1019 (1), 1038 (2 sh), 1073 (1 b), 1106 (0 b), 1174 (0), 1210 (2 sh), 1243 (1), 1300 (1 db. b), 1344 (1), 1399 (2 b), 1454 (4 b), 2213 (10 v. b), 2875 (10 b), 2915 (1), 2937 (3), 2966 (2).

$Cl_3Si-CH_2-CH_2-CH_3$: 170 (3 b), 208 (3 sh), 224 (1 b), 284 (1), 336 (8), 385 (1 b), 425 (0), 455 (5), 475 (10), 512 (0), 565 (1 b), 586 (0 b), 620 (0), 696 (0), 755 (2), 810 (0), 838 (0), 878 (0), 898 (1), 1008 (0), 1030 (4), 1069 (1), 1100 (0), 1147 (0), 1171 (0), 1205 (2), 1239 (0), 1259 (0), 1272 (0), 1405 (1), 1447 (3), 2870 (5), 2887 (2), 2910 (4), 2934 (4), 2964 (2).

$H_2ClSi-CH_2-CH=CH_2$. 249 (0 b), 409 (5 b), 513 (8 db. b), 557 (1), 605 (4 sh), 699 (5 b), 756 (4), 795 (0 b db.), 856 (0), 913 (1), 950 (4), 1000 (0), 1117 (0), 1167 (6 b db), 1188 (1), 1302 (8), 1400 (2 b), 1423 (2), 1633 (10), 2188 (10 b), 2895 (3 b), 2942 (1), 2978 (1), 3005 (3), 3083 (2).

$HCl_2Si-CH_2-CH=CH_2$: 157 (2), 173 (3), 191 (1 b), 240 (2), 270 (1 b), 350 (0 b), 408 (2 b), 495 (10 b), 561 (3 b), 604 (1 b), 650 (0 b), 694 (3), 754 (4), 810 (2 b), 851 (1 b), 911 (2 b), 935 (1), 999 (1), 1113 (0 b), 1168 (5 b), 1189 (2), 1300 (8 sh), 1386 (2), 1417 (3), 1632 (10 sh), 2212 (10 v. b), 2887 (8), 2930 (2 b), 2975 (3 sh), 3005 (8), 3084 (4).

$Cl_3Si-CH_2-CH=CH_2$; 158 (5), 179 (4), 214 (4), 226 (3), 301 (1), 403 (3 b), 453 (10), 576 (2 b db), 766 (2), 922 (1 b), 991 (0), 1178 (7 b), 1302 (8 sh), 1389 (2), 1412 (3), 1634 (10 sh), 2877 (6), 2937 (2), 2983 (2), 3011 (6), 3086 (3).

$H_2ClSi-CH_2-CH-CH_3$: 150 (3), 170 (0 b), 214 (0), 348 (2 b), 414 (0 b), 519 (7 v. b), 690 (4 b), 735 (3),
| 792 (1 b), 833 (1), 855 (0), 954 (5 b), 1040 (1 b), 1101 (2 b), 1161 (1 b), 1217
CH_3 (2 v.b), 1296 (1), 1331 (2 b), 1403 (1), 1450 (4 b), 1463 (4), 2177 (10 b), 2868
(10), 2903 (2), 2933 (3), 2961 (8).

*Determined with an ISP-51 apparatus with a central camera. The intensities are expressed on a 10-grade scale.

HCl$_2$Si–CH$_2$–CH–CH$_3$: 151 (1), 167 (3 b), 239 (2 b), 254 (1), 298 (0 b), 343 (3), 398 (1), 423 (1), 508
        | (8 b db), 557 (2 b db), 625 (0), 67 (2 sh), 744 (3 b), 815 (1 b), 844 (1 b), 958 (3),
         CH$_3$ 1042 (2), 1109 (2 b), 1169 (1), 1219 (3), 1297 (0), 1336 (3 b), 1400 (0 b), 1449
(2 b), 1464 (3 b), 211 (8 v. b), 2868 (10), 2910 (3), 2931 (3), 2964 (7).

Cl$_3$Si–CH$_2$–CH–CH$_3$: 150 (3), 170 (3), 205 (5), 217 (1), 247 (0 b), 278 (0 b), 335 (4), 350 (2 sh), 404 (1),
        | 416 (4), 489 (10), 556 (2 b), 592 (1 b), 739 (2 sh), 764 (1), 842 (2 sh), 957 (2 b),
         CH$_3$ 1044 (2 b), 1100 (2 b), 1169 (1 b), 1219 (2), 1333 (2 b), 1395 (2 b), 1449 (2 b),
1464 (3 b), 2873 (10), 2905 (2), 2931 (3), 2964 (7 b).

H$_2$ClSi–CH$_2$–C=CH$_2$: 148 (3), 198 (3), 382 (1 b), 420 (3), 477 (4), 516 (4 b), 537 (2 b), 568 (1), 608 (0),
        | 657 (1), 676 (1), 703 (0 b), 766 (2), 802 (1), 850 (2), 884 (2 b), 948 (4), 976 (1),
         CH$_3$ 1007 (2), 1071 (0), 1123 (5 b), 1172 (5 v. b), 1219 (0 b), 1278 (2), 1393 (2),
1415 (4 b), 1644 (10), 2183 (10 db), 2881 (4), 2913 (5), 2937 (2), 2983 (4 b), 3079 (2).

HCl$_2$Si–CH$_2$–C=CH$_2$: 148 (1), 169 (4), 207 (0), 241 (3), 383 (0 b), 426 (2 b), 470 (7), 494 (3), 526 (3),
        | 565 (1 b), 656 (0 b), 676 (1 b), 717 (1 b), 765 (2), 814 (2), 834 (2), 853 (2), 892
         CH$_3$ (2 b), 980 (0), 1007 (1), 1117 (3 b), 1175 (3 v. b), 1219 (0 b). 1278 (2 b), 1320 0 b),
1390 (3 b), 1419 (3 b), 1453 (2 b), 1645 (10), 2212 (8 b), 2890 (5 b), 2916 (5), 2940 (3), 2986 (4), 3082 (3).

Cl$_3$Si–CH$_2$–C=CH$_2$: 152 (4), 170 (2), 217 (4), 261 (2), 294 (0), 417 (7), 454 (9), 526 (2), 577 (1 b), 593
        | (1 b), 683 (1), 760 (1), 792 (1), 847 (2), 898 (0), 1129 (2 b), 1186 (2 b), 1279 (1 b),
         CH$_3$ 1396 (2 b), 1430 (1), 1649 (10), 2885 (4), 2927 (3 b), 2992 (3 b), 3085 (2 b).
Examination of the spectra confirms the structures ascribed to the products.

The spectra of chloropropylsilane, dichloropropylsilane, and trichloropropylsilane contained frequencies of 1030, 1070, 1200, and 1450 cm^{-1}, which are characteristic for the group Si–CH$_2$CH$_2$CH$_3$ and have been observed previously in the spectra of trialkylpropylsilanes [16]. The spectra of allylchlorosilane, allyldichlorosilane, and allyltrichlorosilane contained frequencies of 1300, 1395, 1632, 3005, and 3080 cm^{-1}, which are characteristic for the group Si–CH$_2$–CH=CH$_2$ [18]. The spectra of chloro-, dichloro-, and trichloro-(2-methylallyl)silanes contained frequencies of 1278, 1395, 1420, 1645, 2985, and 3080 cm^{-1}, which are characteristic for the group Si–CH$_2$–C=CH$_2$ [19]. In the spectra of all three chloroisobutylsilanes we observed a stable group
                  |
             CH$_3$

of frequencies 954, 1040, 1101, 1168, 1218, 1333, 1400, 1450, and 1464 cm^{-1}, which clearly belong to the vibrations of a silicon-attached isobutyl group.

Irrespective of the character of the silicon-attached group, the spectra of all compounds containing the H$_2$ClSi grouping contained frequencies of 515 (valence vibration of Si–Cl) and 2180 cm^{-1} (valence vibration of Si–H). When we pass to HCl$_2$Si we find that the Si–H frequency rises to 2215 cm^{-1} and the Si–Cl frequency falls to 500 cm^{-1}. An intense line in the 450-480 cm^{-1} region is characteristic for compounds of the type Cl$_3$SiR (symmetrical valence vibration of Si–Cl in the SiCl$_3$ group).

All the spectra given above were determined and analyzed by L. A. Leites, to whom the authors express their thanks.

SUMMARY

1. The disproportionation of alkyl(and alkenyl)dichlorosilanes in presence of pyridine or adiponitrile as catalyst can be used as a method for the synthesis of alkyl(and alkenyl)monochlorosilanes.

2. It was found that the rate of the disproportionation of the alkyl(and alkenyl)dichlorosilanes depends on the character of the hydrocarbon group attached to silicon, and it was shown that it is greatest in the case of alkenyl groups having the double bond in the γ-position with respect to the silicon atom.

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*Original Russian pagination. See C. B. Translation.

β-LACTAMS

COMMUNICATION 3. REACTION MECHANISM

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We previously reported a new method of preparing β-lactams from amides of β-halo acids under the action of potassium or sodium amide in liquid ammonia [1]. This method is relatively simple and the starting materials are accessible; it opens up wide possibilities for the synthesis of various β-lactams. The procedure in the synthesis of β-lactams can be considerably simplified by carrying out the reaction in various organic solvents under the action of a suspension of potassium hydroxide powder or of aqueous solutions of caustic alkalis (Table 1). Aliphatic ketones were found to be particularly effective solvents; in these, β-lactams were formed in even higher yields than in liquid ammonia. On the other hand, performance of the reaction in alcohols, or even dilution of another solvent with a little alcohol, sharply reduces the yield of β-lactam. Replacement of potassium hydroxide by sodium or lithium hydroxide has only a slight effect on reaction rate and does not affect the general direction of the reaction. However, the use of a tertiary amine or an alkoxide as alkaline agent completely prevents the formation of a β-lactam (Table 2).

In explanation of the mechanism of the conversion of β-halo acid amides into β-lactams a scheme was proposed which consisted of two stages: 1) enolization of the amide with formation of a salt of the imide form; 2) intramolecular nucleophilic attack of the β-carbon by nitrogen atoms carrying an unshared electron pair; as a result a bromide ion is liberated and ring closure occurs:

$$
\begin{array}{c}
\underset{\underset{\displaystyle R'NH-C=O}{|}}{RCHBrCH_2} \xrightarrow{KNH_2} \underset{\underset{\displaystyle R'N=C-O-K}{|}}{RCHBrCH_2} \\[3em]
\underset{\underset{\displaystyle R'N=C-O-K}{|}}{\overset{\overset{\displaystyle Br}{|}}{RCH}-CH_2} \longrightarrow \underset{\underset{\displaystyle R'-N-C=O}{\quad|\qquad|}}{RCH-CH_2}
\end{array}
\tag{1}
$$
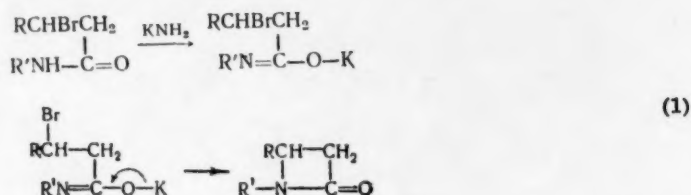
It follows from this scheme that amides not prone to the enolization characteristic of carboxamides will not cyclize. It was, in fact, found that all attempts to convert 1,2-dibromo-N-cyclohexyl-2-phenylethanesulfonamide (which was taken as an example)* into its β-sultam were unsuccessful. The only reaction product was always β-bromo-N-cyclohexyl-β-styrenesulfonamide:

$$
\begin{array}{c}
C_6H_5CHBrCHBr \\
\underset{C_6H_{11}NH \cdot SO_2}{|}
\end{array} \rightarrow C_6H_5CH{=}CBrSO_2NHC_6H_{11}
$$
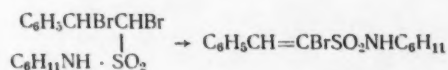
These results confirm that the first stage of the reaction is the enolization of the original amide.

*Unlike carboxamides, sulfonamides do not enolize [2].

TABLE 1

Reaction of $C_6H_5CHBrCH_2CONHC_6H_5$ with KOH Powder in Various Solvents

Solvent	Yield (%)			Solvent	Yield (%)		
	β-lactam	unsaturated amide	β-amino acid		β-lactam	unsaturated amide	β-amino acid
Butanone	88.6	7.0	—	Acetone 87.5% Methanol 12.5%	—	68.0	10.0
Acetone	68.0	Not determined	15				
Benzene	41.0	32.0	—	Acetone 50% Water 50%	57.0	27	—
Hexane	22.0	77	—				
N,N-Dimethylformamide	57.4	29.5	—				
Diethyl ether	35.0	45.0	—	Acetone 50% Benzene 50%	68.0	14.0	—
Dioxane	43.0	56.0	—				
Tetrahydrofuran	37.8	62.0	—	Acetone 50% Hexane 50%	72.0	15.0	—
Methanol	—	88.6	—				
Ethanol	—	86.0	—				
Butyl alcohol	—	91.0	—	Acetone 50% Diethyl ether 50%	68.0	15.7	—
Liquid ammonia	81.0	—	—				
				Dioxane 70% Water 30%	60	34	—
Acetone 87.5% Ethanol 12.5%	—	36.0	35.0	Tetrahydrofuran 50% Water 50%	51.0	44.0	—
Acetone 50% Ethanol 50%	—	79.5	—	Ethanol* 70% Water 30%	—	95.4	—

* The reaction was carried out with LiOH.

The rate at which the β-lactam ring is closed may depend on two factors: the acidity of the original amide, which is responsible for the first stage of the reaction, and the reactivity of the intermediate bromo amide ion, which determines the second stage of the process. Substituents of the "first kind" [CH_3, CH_3O, $(CH_3)_2N$, etc.] introduced into the para position of the aryl group attached to nitrogen are favorable to the second stage of the reaction, which requires the presence on the nitrogen atom of an electron density sufficient to bring about the nucleophilic attack of the β-carbon atom. However, substituents of the "second kind" (NO_2, COOR, CN, etc.), which increase the acidity of the original amide but lower the electron density on the nitrogen atom, must hinder the second stage of the reaction but accelerate the second stage.

The reaction was carried out in aqueous dioxane solution under the action of lithium hydroxide at 0°. The rate of the process was estimated from the amount of bromide ion formed (Table 7). In view of the fact that closing of the β-lactam ring was accompanied by dehydrohalogenation of the original amide with formation of a substituted cinnamamide, the yield of β-lactam was determined in some cases from the amount of amino acid formed by hydrolysis of the reaction products. Also, a study was made of the kinetics of the reaction occurring in alcoholic solution, the only product of which was a derivative of cinnamamide (Table 9). Both these reactions were to be of second order, and their rate constants were close in value. Increase in the concentration of alkali or amide greatly accelerated the reactions, while having no effect on the rate constant [mechanism of a bimolecular reaction (Sn 2)].

Of all the compounds studied, cyclization occurred most rapidly with β-bromo-4'-nitrocinnamanilide. The resulting β-lactam was less stable than other 2-azetidinones that we prepared; this was indicated by the
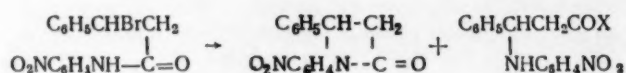
TABLE 2

Effect of the Nature of the Alkaline Agent on the Cyclization of β-Bromo-
hydrocinnamanilide in Homogeneous Acetone Solution

Alkaline agent	Yield of	
	$C_6H_5CH-CH_2$ | | $C_6H_5N - C=O$ in %	$C_6H_5CH=CHCO$ | C_6H_5NH in g
Aqueous 0.25 N KOH	67.4*	18.6
Aqueous 0.25 N NaOH	65*	15.0
Aqueous 0.25 N LiOH	66.6	16.6
Triethylamine	—	93.0
Triton B	72.3**	13.6
0.43 N dioxane solution of C_2H_5ONa	—	65.0

* The yield of β-lactam was determined after separation of the reaction
products by fractional crystallization.
** The yield of β-lactam was determined from the amount of β-amino
acid formed by hydrolysis of the reaction product.

isolation from the reaction mixture not only of 1-p-nitrophenyl-4-phenyl-2-azetidinone, but also of appreciable
amounts of its decomposition products.

$$C_6H_5CHBrCH_2 \qquad\qquad C_6H_5CH-CH_2 \qquad C_6H_5CHCH_2COX$$
$$\mid \qquad\qquad\qquad \mid \quad\; \mid \qquad\qquad \mid$$
$$O_2NC_6H_4NH-C=O \;\rightarrow\; O_2NC_6H_4N--C=O \;+\; NHC_6H_4NO_2$$

The slowest to react was β-bromo-4'-methoxyhydrocinnamanilide. Hence, substituents of the first kind
retard cyclization and substituents of the second kind accelerate it (Table 3). Analogous effects of substituents
of the first and second kind were observed in an investigation on the rate of the formation of a pyrrolidinone
ring from N-aryl-4-bromobutyramides [3]. All this indicates that the deciding factor in the rate of closure of
a β-lactam ring is the acidity of the original amide, which facilitates the first stage of the reaction, namely
formation of the salt of the imide form of the amide.

EXPERIMENTAL

Preparation of β-lactams by the action of KOH powder in organic solvents. Potassium hydroxide powder
(1 g) was added to a weighed amount of the amide (0.002 mole) in 40 ml of solvent. The mixture was shaken
for one hour, after which solvent was evaporated off to dryness. The residual solid reaction mixture was washed
with dilute HCl and water, dried, and usually separated by fractional crystallization (Tables 4 and 5).

Preparation of β-lactams in a homogeneous medium. To a weighed amount of the amide (0.002 mole)
dissolved in a mixture of 70 ml of acetone and 14 ml of water, 16 ml of 0.25 N aqueous caustic alkali (0.004
mole) was added. The homogeneous reaction mixture was left for one hour, and the solvent was then evapor-
ated off. The solid reaction product was treated further as described above.

N-Cyclohexyl-β-styrenesulfonamide (IV). In the reaction of cyclohexylamine with β-styrenesulfonyl
chloride (III), not only (IV), but also the hydrochloride of N-cyclohexyl-2-cyclohexylamino-2-phenylethane-
sulfonamide (V) is formed. We did not succeed in bringing about the addition of cyclohexylamine to (IV), or
to the sodium salt or ethyl ester of β-styrenesulfonic acid, from which it follows that the addition of cyclo-
hexylamine to (III) and the formation of (IV) proceed simultaneously:

$$C_6H_5CH=CHSO_2Cl + NH_2C_6H_{11}-\Big\langle$$

$$C_6H_5CH=CHSO_2NHC_6H_{11} \qquad\qquad\text{(IV)}$$

$$C_6H_5CH-CH_2$$
$$\mid \qquad\quad \mid$$
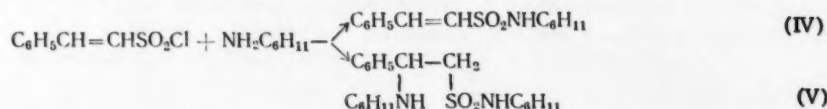$$C_6H_{11}NH \quad SO_2NHC_6H_{11} \qquad\qquad\text{(V)}$$

TABLE 3

Rate of Reaction of Arylamides of β-Bromohydrocinnamic Acid with LiOH in Aqueous Dioxane Solution (Concentration of bromo amide, 0.01 mole/liter)

Amount of amide that reacted (% of original) / Arylamide	Amount (%) of amide that reacted in the course of					Yield of β-lactam after 60 min (%)
	2 min	4 min	10 min	30 min	60 min	
$C_6H_5CHBrCH_2$ / $CH_3OC_6H_4NHCO$	22,0	30,5	46,5	—	—	52,5
$C_6H_5CHBrCH_2$ / $CH_3C_6H_4NHCO$	24,0	34,0	50,0	—	—	57,0
$C_6H_5CHBrCH_2$ / C_6H_5NHCO	35,0	44,5	•65,2	—	—	60,4
$C_6H_5CHBrCH_2$ / $C_2H_5OCOC_6H_4NH—CO$	79,0	—	95,0	98,5	99,5	—
$C_6H_5CHBrCH_2$ / BrC_6H_4NHCO	56,3	—	81	—	—	—
$C_6H_5CHBrCH_2$ / $O_2NC_6H_4NHCO$	98,0	—	—	100	—	—

A solution of 13.5 g of cyclohexylamine in 10 ml of benzene was added gradually to a solution of 13.7 g of β-styrenesulfonyl chloride (III) in 30 ml of benzene. The crystals remaining after the evaporation of benzene were washed with water and dilute hydrochloric acid, and were recrystallized from absolute alcohol. We obtained 7.8 g (45%) of N-cyclohexyl-β-styrenesulfonamide (IV), m. p. 114-115° (found: C 63.24; H 7.26; S 12.15%. $C_{14}H_{19}NO_2S$. calculated: C 63.41; H 7.17; S 12.1%), and 3.3 g (16.5%) of the hydrochloride of N-cyclohexyl-2-cyclohexylamino-2-phenylethanesulfonamide (V), m. p. 217-218° (found: C 59.91; H 8.38%. $C_{20}H_{33}NO_2SO_2$. calculated: C 59.92; H 8.24%.

When treated with aqueous alkali, (V) gave N-cyclohexyl-2-cyclohexylamino-2-phenylethanesulfonamide, m. p. 115-116° (from alcohol). Found: C 65.98; H 8.89; S 8.86%. $C_{20}H_{32}NO_2O_2$. Calculated: C 65.93; H 8.79; S 8.79%.

1,2-Dibromo-N-cyclohexyl-2-phenylethanesulfonamide (I). A 10% solution of bromine in glacial acetic acid (8 ml) was added to a solution of 1.35 g of (IV) in 50 ml of glacial acetic acid, and the mixture was left for three hours in sunlight. Solvent was distilled off, and the residue was recrystallized from alcohol. We obtained 1.7 g (78%) of crystals of (I), m. p. 127-129°. Found: C 39.64; H 4.49%. $C_{14}H_{19}Br_2SNO_2$. Calculated: C 39.53; H 4.47%.

β-Bromo-N-cyclohexyl-β-styrenesulfonamide (VI). a) We added 1.1 g of (I) to a suspension of 0.25 g of potassium hydroxide in liquid ammonia. On the next day ammonia was evaporated off, and the residue was washed with water and recrystallized from absolute alcohol. We obtained 0.85 g (94%) of crystals of (VI), m. p. 116-117°. Found: C 49.15; H 5.29%. $C_{14}H_{18}NSO_2Br$. Calculated: C 48.84; H 5.23%.

When (VI) was heated with excess of zinc dust in 80% ethyl alcohol, a bromine atom was replaced by hydrogen and an 80% yield of crystals of m. p. 114-115° was obtained; in admixture with (IV) they showed no depression of melting point.
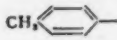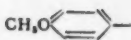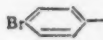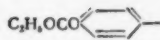
b) To a solution of 0.5 g of (I) in 20 ml of absolute alcohol, 1.5 ml of a 1 N solution of potassium hydroxide in absolute alcohol was added. After 10 minutes water was added and the precipitated crystals were filtered off. We obtained 0.28 g (70%) of crystals, m. p. 116-117° (from alcohol) and identical with (VI).

c) To a suspension of 0.5 g of potassium hydroxide in 20 ml of acetone, 0.53 g of (I) was added and the mixture was stirred for one hour. The acetone was evaporated off, and the residue was washed with water and recrystallized from alcohol. We obtained 0.2 g (50%) of crystals, m. p. 116-117° and identical with (VI).

TABLE 4

β-Lactams Prepared by the Action of KNH_2 in Liquid NH_3 by the Method Described in the Preceding Communication [1]
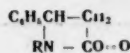
$$C_6H_5CHBrCH_2CONHR \nearrow \begin{array}{c} C_6H_5CH-CHCONHR \ (II) \\ \searrow C_6H_5CH-CH_2 \ + \ C_6H_5CH-CH_2COOH \\ \quad | \qquad | \qquad \qquad | \\ \quad RN-C=O \ (I)^* \qquad RNH \qquad (III)^* \end{array}$$

No.	R	Yield (%)			Notes
		(I)	(II)	(III)	
1	CH_3◯—	81.3	8.4	3.0	The reaction product was washed with water (on acidification with an aqueous solution of CH_3COOH the amino acid separated) and a little ether; it was then recrystallized from alcohol. The β-lactam was obtained. When the mother liquor was diluted with water, p-cinnamotoluidide separated
2	CH_3O◯—	84.1			The reaction product was washed with water and recrystallized from isopropyl alcohol
3	Br◯—	63.0	13.0	21.0 resinous residue	After being washed with water and ether, the solid product was recrystallized from alcohol. The β-lactam was isolated. On hydrolysis of part of the reaction product with alcoholic KOH, water-insoluble 4'-bromocinnamanilide was isolated
4a	C_2H_5OCO◯—	66.0	10.6	—	The reaction product was washed with water (on acidification of the aqueous solution with CH_3COOH, product 4b was isolated) and ether, and it was recrystallized from alcohol. Product 4a was isolated. Treatment of product 4a with 1 M alcoholic alkali resulted in hydrolysis of the ester group and formation of product 4b.
4b	HOCO◯—	22.8			
5	NO_2◯—	54.0	16.6	11.0 of amide of β-amino acid	Ammonia was evaporated off rapidly; the residue was washed with conc. HCl (when alkali was added the amide of the β-amino acid separated) and crystallized from ethyl acetate. This gave 4'-nitrocinnamanilide. The β-lactam was isolated from the mother liquor
6	◯◯	63.0	—	—	

* It should noted that compounds (I) and (III) in this table differ from the compounds denoted by (I) and (III) in the text — Publisher.

Preparation of arylamides of β-bromohydrocinnamic and cinnamic acids. With the exception of the p-bromoanilide of β-bromohydrocinnamic acid, all the arylamides were synthesized by the usual method, as given in the previous paper [1] (Table 6).

TABLE 5

Properties of β-Lactams

$$C_6H_5CH-CH_2$$
$$RN-CO-O$$

R	M. p. (°C) (from solvent indicated)	C (%) found	C (%) calculated	H (%) found	H (%) calculated	N (%) found	N (%) calculated
CH₃—⟨ ⟩—	126—128, alcohol	80,83	81,0	6,36	6,37	5,72	5,89
CH₃—⟨ ⟩—	95—97, isopropyl alcohol	75,62	75,88	5,90	5,88	Br	
Br—⟨ ⟩—	124—126, isopropyl alcohol	59,28	59,63	3,94	3,97	25,99	26,49
C₂H₅OCO—⟨ ⟩—	137—138, alcohol	73,26	73,22	5,79	5,76	4,75	4,74
NO₂—⟨ ⟩—	132—134, alcohol	67,40	67,39	4,34	4,40	10,74	10,07
⟨naphthyl⟩	188—189, alcohol	83,43	83,88	5,64	5,50	5,05	5,12

TABLE 6

Synthesized Arylamides (a) of β-Bromohydrocinnamic Acid $C_6H_5CHBrCH_2CONHR$ and (b) of Cinnamic Acid

R	M. p. (°C) (from solvent indicated)	C (%) found	C (%) calculated	H (%) found	H (%) calculated	Br (%) found	Br (%) calculated	N (%) found	N (%) calculated
a) CH₃—⟨ ⟩—	127—128, alcohol	60,05	60,37	5,10	5,03	25,53	25,16		
b)	162—163,5, aq. alcohol							5,89	5,90
a) CH₃O—⟨ ⟩—	128—129, alcohol	57,47	57,49	5,03	4,79				
b)	154—155, isobutyl alcohol	75,87	75,88	5,92	5,92				
a) Br—⟨ ⟩—	204—205, absolute alcohol	47,06	47,00	3,49	3,40	41,58	41,77		
b)	190—192, isopropyl alcohol	59,56	59,6	3,89	3,97	26,13	26,49		
a) C₂H₅OCO ⟨ ⟩—	144—145, alcohol	57,45	57,44	4,79	4,78	21,23	21,29		
b)	171—172, aq. alcohol	73,10	73,22	5,78	5,76			4,90	4,75
a) NO₂—⟨ ⟩	207—210, alcohol	51,99	51,57	3,81	3,72	22,35	22,92		
b)	222—224, alcohol							10,44	10,44
a) ⟨naphthyl⟩	191—193, absolute alcohol							4,03	3,95
b)	179—180, alcohol							5,14	5,12

β,4'-Dibromohydrocinnamanilide. A mixture of 5 g (0.016 mole) of β-bromohydrocinnamanilide and 4.3 g (0.024 mole) of N-bromosuccinimide in 160 ml of carbon tetrachloride was refluxed for 12 hours. When the solution was cool there separated 5 g (80%) of product of m. p. 204-205° (from alcohol) and corresponding in analysis to the compound $C_6H_5CHBrCH_2CONHC_6H_4Br$.

TABLE 7

Rates of Reaction of Arylamides of β-Bromohydrocinnamic Acid with LiOH in 70% Dioxane (concentration of original amide 0.01 mole/liter)

Arylamide	Reaction time (min)	Amount of amide that reacts (%)	K_2 (liter/ mole·min)	Arylamide	Reaction time (min)	Amount of amide that reacts (%)	K_2 (liter/ mole·min)
C$_6$H$_5$CHBrCH$_2$ CH$_3$OC$_6$H$_4$NH–CO	2,00 4,00 7,00 10.00	22,0 30,5 38,0 46,5	— 10,9 8,7 8,8	C$_6$H$_5$CHBrCH$_2$ COC$_6$H$_4$NHCO OC$_2$H$_5$	2,00 10,00 30,00 60,00	79,0 95,0 98,5 99,5	— — — —
C$_6$H$_5$CHBrCH$_2$ CH$_3$C$_6$H$_4$NH–CO	2,00 4,00 7,00 10,00	24,0 34,0 42,0 50,0	— 12,6 10,3 10,9	C$_6$H$_5$CHBrCH$_2$ BrC$_6$H$_4$NHCO	2,00 5,00 10,00 20,00	56,5 73,8 81,0 87,0	— — — —
C$_6$H$_5$CHBrCH$_2$ C$_6$H$_5$NHCO	2,00 4,18 7,25 10,25	35,0 44,5 56,5 65,2	— 19,4 18,0 18,2	C$_6$H$_5$CHBrCH$_2$ NO$_2$C$_6$H$_4$NHCO	2,00 30,00	98,0 100,0	— —

TABLE 8

Rates of Reaction of Arylamides of β-Bromohydrocinnamic Acid with LiOH in Alcohol (Formation of Arylamides of Cinnamic Acid) (Concentration of original amide 0.01 mole/liter)

Arylamide	Reaction time (min)	Amount of amide that reacts (%)	K_2 (liter/ mole·min)	Arylamide	Reaction time (min)	Amount of amide that reacts (%)	K_2 (liter/ mole·min)
C$_6$H$_5$CHBrCH$_2$ C$_6$H$_5$NHCO	2,00 3,50 7,00 10,00	35,0 43,5 55,5 65,0	— 20,1 18,0 18,5	C$_6$H$_5$CHBrCH$_2$ CH$_3$OC$_6$H$_4$NHCO	2,25 4,50 7,09 10,09	31,0 39,0 54 76	— 14,4 16,2 —

Determination of the rates of reaction of β-bromohydrocinnamanilides with alkaline agents in a homogeneous medium. A weighed amount of anilide (0.001 mole) was introduced into a mixture of 70 ml of solvent and 26 ml of water. The solution was cooled to 0° in a thermostat, and rapid addition was made of 4 ml of 0.25 N aqueous caustic alkali; 20 ml samples were then pipetted from the reaction mixture at definite intervals of time.

The sample of reaction solution was introduced into a separating funnel containing 10 ml of 30% HNO$_3$, 20 ml of water, and 20 ml of chloroform; the mixture was shaken vigorously, and the chloroform layer was separated. The aqueous solution was treated with a further 20 ml of chloroform, which was separated and transferred to a flask for titration. Both chloroform extracts were washed with 10 ml of water, which was then added to the main aqueous solution. The bromide ion was determined by the Volhard method. For this purpose 10 ml of 0.05 N AgNO$_3$ was added to the test sample, and unchanged silver ion was back-titrated with 0.05 N NH$_4$SCN in presence of ferric ammonium alum (see Tables 7 and 8).

TABLE 9

β-Amino Acids Obtained by the Hydrolysis of β-Lactams

$$C_6H_5CH-CH_2 \quad C_6H_5CH-CH_2COOH$$
$$| \quad | \rightarrow \quad |$$
$$RN-C\cdots O \quad RNH$$

R	M.p. (°C) (from solvent indicated)	C (%)		H (%)		N (%)	
		found	calcu-lated	found	calcu-lated	found	calcu-lated
CH₃〈 〉—	136—137 alcohol	74,65	75,29	6,53	6,66	5,83	5,49
Br〈 〉—	136—138 alcohol	56,21	56,25	4,40	4,38	24,96	25,00
HOCO〈 〉—*	183—187, aq. alcohol	66,65	67,37	5,42	5,26		
NO₂〈 〉—**						8,53	8,64
NO₂〈 〉—***	147—148, chloroform	63,14	63,16	5,56	5,26	15,43	14,75
〈 〉	164—165, benzene-petro-leum ether	78,29	78,35	5,90	5,84	4,87	4,81

* In the hydrolysis of 1-p-(ethoxycarbonyl)phenyl-4-phenyl-2-azetidinone, in addition to ring-opening, hydrolysis of the ester group occurs with formation of a product containing a free carboxy group in the para position to nitrogen.
** Potassium salt of amino acid.
*** Amide of amino acid.

As the bromide ion may be liberated in two competing reactions, namely the formation of the β-lactam and the formation of a substituted cinnamamide, at the same intervals of time and concurrently with the taking of samples for Volhard titration, the yield of β-lactam was determined by hydrolysis of the reaction product and quantitative isolation of the β-amino acid (Table 9).

SUMMARY

1. The cyclization of amides of β-halo acids to β-lactams is a second-order reaction which has a bimolecular-substitution mechanism.

2. Substituents of the "second kind" meta-orienting in the para position in the nitrogen-attached aryl group accelerate the reaction, whereas substituents of the "first kind" (ortho-para-orienting) retard it; the reaction rate is determined by the acidity of the original amide.

3. The synthesis of β-lactams is considerably facilitated by the use of organic solvents instead of liquid ammonia.

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CHEMISTRY OF 1,3-CYCLOHEXANEDIONE

COMMUNICATION 3. SYNTHESIS AND ANTIHELMINTHIC ACTION OF
1,3-CYCLOHEXANEDIONE DERIVATIVES CONTAINING BRANCHED
ALIPHATIC CHAINS

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1,3-Cyclohexanedione derivatives containing long branched chains have not been described previously in the literature. Such compounds, however, are of interest on account of their possible biological activity. We found that 1,3-cyclohexanedione can be alkylated in about 50% yield by branched allyl bromides, which were prepared earlier by Nazarov and co-workers [1]. In this way we synthesized 2-(3,7-dimethyl-2-octenyl)-1,3-cyclohexanedione (IV), 2-(3,7-dimethyl-2,6-octadienyl)-1,3-cyclohexanedione (V), and 2-(3,7,11-trimethyl-2-dodecenyl)-1,3-cyclohexanedione (VI), which were converted smoothly into the corresponding enol acetates (VII), (VIII), and (IX) when treated at the boil with acetic anhydride.

$$CH_2=CH-C(OH)(CH_3)R$$
$$(I)-(III)$$
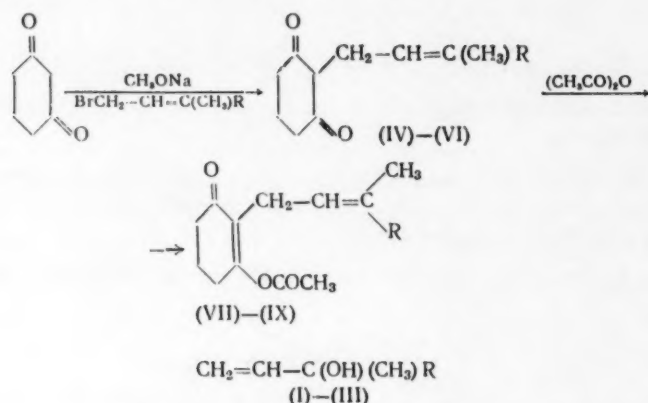
(I), (IV), (VII), $R = (CH_2)_3 CH (CH_3)_2$

(II), (V), (VIII), $R = (CH_2)_2 CH = C (CH_3)_2$

(III), (VI), (IX), $R = (CH_2)_3 CH (CH_3)(CH_2)_3 CH (CH_3)_2$

When tested in vitro on ascarids of pigs (nematoda) by previously described methods [2], the compounds (IV)-(IX) showed definite activity in saturated solutions (less than 10 p.p.m.).* The highest activity was shown
* The tests on the antihelminthic activities and toxicities of the preparations were carried out by A. I. Krotov.

by the enol acetate (IX), which in ascarids produced convulsive contractions of the body alternating with periods of depression. A similar effect is shown by such antihelminthics as santonin and piperazine [3]. In the mechanism of its action on ascarids the enol acetate differs from these last preparations, and in this connection it presents special interest.

The enol acetate is an oily liquid with a pleasant odor reminiscent of vinegar; it is almost tasteless and leaves no unpleasant sensations in the mouth. In a dose of 5 g per kg of animal, cats and white mice take the enol acetate without visible pathological effects; only a laxative action is observed, and this permits the use of the preparation without an accompanying dose of a laxative. The enol acetate was tested in the toxocarosis of cats and the syphaciosis and trichocephaliasis of white mice. Of ten cats infected with toxocarae, nine were completely freed from infection by an enol acetate dose of 0.5 g per kg; in all,94% of the nematodes were removed. In the syphaciosis and trichocephaliasis of mice the preparation was given in a dose of 2.5 g per kg; the dissection of treated and control animals was carried out on the third day after the treatment. In the case of syphaciosis the preparation was given to 15 animals; after treatment three nematodes were found, all in one mouse. In the 15 control mice we found 168 syphaciae, so that we may consider that 98.2% of the nematodes were removed. In the case of trichocephalaisis the preparation was given to ten animals; in the treated group we found 88 examples of trichocephalids, but in the ten control mice we found 681, so that we may consider that 87.1% of the nematodes were removed.

We may conclude from these results that the enol acetate (IX) may be an effective antihelminthic in the ascaridosis, enterobiasis, andtrichocephaliasis of human beings, and also in various nematodoses of animals. The greatest interest lies in the possibility of its use in trichocephaliasis in view of the fact that for the treatment of this condition there are, as yet, no preparations that are effective and of low toxicity.

A communication has recently appearedconcerning the good results obtained by the treatment of the trichocephaliasis of human beings with dithiazanine [4], which was also found to be highly effective in laboratory animals in syphaciosis, ascaridosis, strongyloidoses, and trichocephaliasis [5]. By the use of dithiazanine in the trichocephaliasis of mice in a dose of 0.012 g per kg per day for three days we brought about the removal of only 27% of the nematodes.

EXPERIMENTAL

The branched allyl bromides were prepared by the action of hydrogen bromide on the corresponding tertiary alcohols: 3,7-dimethyl-1-octan-3-ol (I) [b. p. 68-69° (6 mm); $n^{20}D$ 1.4390, 3,7-dimethyl-1,6-octadien-3-ol (II) [b. p. 80-82° (10 mm); $n^{20}D$ 1.4622], and 3,7,11-trimethyl-1-dodecen-3-ol (III) [b. p. 98-99° (2 mm); $n^{20}D$ 1.4490] [1]. The allyl bromides were used in the alkylation reactions without purification.

2-(3,7,11-Trimethyl-2-dodecenyl)-1,3-cyclohexanedione (VI). Hydrogen bromide (20 g) was passed at −10° into 50.6 g of 3,7,11-trimethyl-1-dodecen-3-ol (III), and the mixture was stirred for two hours at room temperature, washed with saturated sodium bicarbonate solution and with water, and dried with magnesium sulfate. The resulting allyl bromide, without further purification,was added to the sodium derivative of 1,3-cyclohexanedione, which was prepared from 25 g of 1,3-cyclohexanedione and 5.1 g of sodium in 250 ml of methanol. After the mixture had stood for one hour at room temperature, it was boiled for two hours and methanol was distilled off. The alkaline solution was acidified with dilute hydrochloric acid, and there was a precipitate of 22.5 g of the dione (VI), which melted at 74-76° after crystallization from 80% methanol. Found: C 78.63; 78.79; H 11.29; 11.40%. $C_{21}H_{38}O_2$. Calculated: C 78.70; H 11.32%.

The enol acetate (IX). A mixture of 10.7 g of the above-described dione (VI) and 50 ml of acetic anhydride was boiled for one hour; excess of acetic anhydride was distilled off, and the residue was vacuum distilled. We obtained 9.2 g of the enol acetate (IX), b. p. 171-176° (0.05 mm) and $n^{20}D$ 1.4855. Found: C 75.65; 75.61; H 10.41; 10.31%. $C_{22}H_{40}O_3$. Calculated: C 76.20; H 10.56%. 2,4-dinitrophenylhydrazone had m. p. 101-102° (from methanol), λ_{max} 368 mμ (heptane). Found: N 10.51; 10.59%. $C_{28}H_{44}O_6N_4$. Calculated: N 10.32%.

In an analogous way we prepared the diones (IV) and (V) and the corresponding enol acetates (VII) and (VIII).

2-(3,7-Dimethyl-2-octenyl)-1,3-cyclohexanediol (IV). This had m. p. 91-104° (from 70% methanol). Found: C 76.26; 76.32; H 10.42; 10.41%. $C_{16}H_{26}O_2$. Calculated: C 76.74; H 10.47%.

The product was probably a mixture of isomers.

The enol acetate (VII). This had b. p. 135-137° (0.05 mm); $n^{20}D$ 1.4892; yield 65%. Found: C 73.72; 73.79; H 9.52; 9.41%. $C_{15}H_{28}O_3$. Calculated: C 73.93; H 9.65%.

Its 2,4-dinitrophenylhydrazone had m. p. 136-136.5° (from methanol); λ_{max} 368.5 mμ (heptane). Found: N 12.70; 12.95%. $C_{24}H_{32}N_4O_6$. Calculated: N 12.41%.

2-(3,7-Dimethyl-2,6-octadienyl)-1,3-cyclohexanedione (V). This had m. p. 101-104° (from aqueous methanol). Found: C 77.25; 77.05; H 9.83; 9.85%. $C_{16}H_{24}O_2$. Calculated: C 77.39; H 9.74%.

The enol acetate (VIII). This had b. p. 140-142° (0.05 mm); $n^{20}D$ 1.5022; yield 70%. Found: C 73.64; 73.63; H 8.82; 8.76%. $C_{18}H_{26}O_3$. Calculated: C 74.44; H 9.02%.

The 2,4-dinitrophenylhydrazone had m. p. 120-121° (from methanol); λ_{max} 368 mμ (heptane). Found: N 12.12; 12.16%. $C_{24}H_{30}N_4O_6$. Calculated: N 11.90%.

The diones (IV), (V), and (VI) readily oxidized when allowed to stand.

SUMMARY

1,3-Cyclohexanedione was alkylated with branched allyl bromides. The resulting 2-alkyl derivatives (IV), (V), and (VI), and also their enol acetates (VII), (VIII), and (IX), have an antihelminthic action. The highest antihelminthic activity is shown by the enol acetate (IX).

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RAMAN-SPECTRUM INVESTIGATION OF SOME SUBSTITUTED
CYCLOHEXANOLS AND THEIR ACETIC ESTERS

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Because of the possibility of axial (a) and equatorial (e) substitution in the cyclohexane ring, the actual number of possible isomers of a disubstituted cyclohexanol is greater than would be permissible on the basis of earlier views on cis-trans isomerism. Accordingly, for 2-methyl-1-vinylcyclohexanol with the cyclohexane ring in the chair form*, one would expect to have two cis conformations (ae, ea) and two trans conformations (aa, ee),** instead of the one cis and one trans configuration predicted by previous theories of cis-trans isomerism [1].
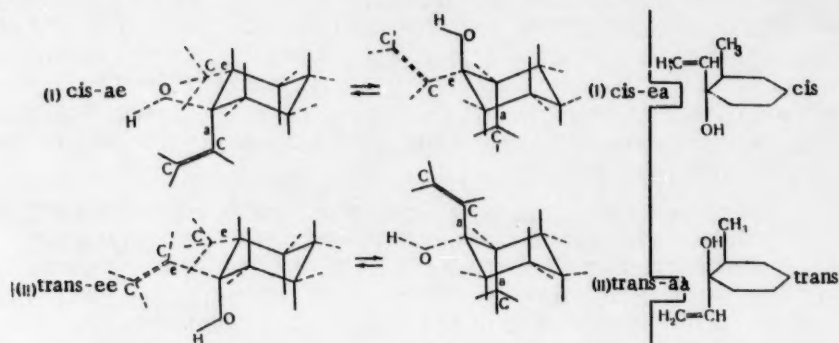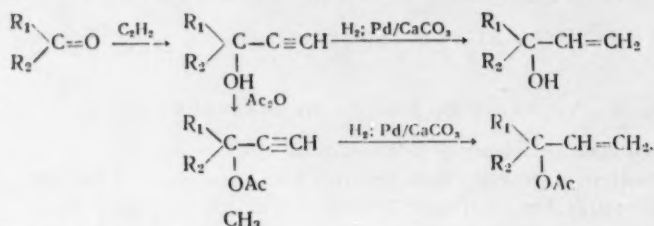

As a result of the different stabilities of different conformations and of some other factors, by no means all of the possible conformations actually exist in the gas and liquid phases; the stable (dominant) ones predominate [1]. It is probable that in the crystalline state there is only one conformation. The physical properties and reactivity of the functional group depend on the position of the group in the conformation (axial or equatorial). The position of the group can sometimes be established chemically, but this can often be done only by physical methods.

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* The chair form of cyclohexane or one of its substitution products is accompanied in the tautomeric mixture by the boat form, the content of which is extremely low at room temperature, though it increases with rise in temperature [1].

** In this paper the conformation is defined in terms of the relative positions of the largest substituents, in this case the methyl and vinyl groups.

In the present investigation we undertook the determination from the Raman spectra of the conformations of cis- and trans-2-methyl-1-vinylcyclohexanols (I) and (II) and of their acetic esters (III) and (IV); of the acetic esters (V) and (VI) obtained from cis- and trans-1-ethynyl-2-methylcyclohexanols; of 1-vinylcyclohexanol (VII) and its acetic ester (VIII); of 1-ethynylcyclohexanol (IX) and its acetic ester (X). Acetylenic alcohols prepared by the Favorskii reaction were hydrogenated over a palladium catalyst to the corresponding ethylenic alcohols. A portion of the acetylenic alcohol was acetylated and then subjected to selective hydrogenation to the corresponding ethylenic acetic ester. The acetylenic alcohols were first separated into their cis and trans isomers in cases in which cis-trans isomerism occurred. The scheme of synthesis was [2]:

$$\begin{array}{c}
R_1 \\
\diagdown \\
R_2
\end{array} C{=}O \xrightarrow{C_2H_2}
\begin{array}{c}
R_1 \\
\diagdown \\
R_2
\end{array} \underset{\underset{\downarrow\ Ac_2O}{OH}}{\overset{|}{C}}{-}C{\equiv}CH \xrightarrow{H_2:\ Pd/CaCO_3}
\begin{array}{c}
R_1 \\
\diagdown \\
R_2
\end{array} \underset{OH}{\overset{|}{C}}{-}CH{=}CH_2$$

$$\begin{array}{c}
R_1 \\
\diagdown \\
R_2
\end{array} \underset{\underset{\underset{CH_3}{\overset{|}{}}}{OAc}}{\overset{|}{C}}{-}C{\equiv}CH \xrightarrow{H_2:\ Pd/CaCO_3}
\begin{array}{c}
R_1 \\
\diagdown \\
R_2
\end{array} \underset{OAc}{\overset{|}{C}}{-}CH{=}CH_2.$$

in which R_1, $R_2 = CH_2(CH_2)_3CH_2$ and $-CH(CH_2)_3CH_2-$.

The physical properties of the products are given in Table 1.

The Raman spectra were determined in the liquid phase with a Soviet ISP-51 spectrograph with a central camera and with Hilger E-612 spectrograph; the exciting radiation was 4358 A blue light from a mercury lamp.*

cis-2-Methyl-1-1vinylcyclohexanol (I), $\Delta\nu$ (cm^{-1}): 170 (1), 181 (1), 251 (2 db), 273 (3*), 284 (3*), 299 (2 db), 363 (3), 353 (2 sh), 376 (3 b), 433 (4*), 443 (4 sh*), 452 (4*), 499 6 db b), 532 (0*), 546 (3* b), 566 (0**), 579 (3**), 680 (2**), 695 (9*), 711 (2*), 801 (3), 821 (2 sh), 839 (5 sh), 865 (4), 890 (1), 925 (3*), 936 (1*), 957 (2), 981 (6*), 998 (6*), 1014 (1*), 1043 (2**), 1056 (3**), 1081 (4**), 1113 (1**), 1137 (1**),1155 (5**), 1177 (5**), 1222 (3 db), 1261 (7b*), 1278 (1*), 1303 (7 b), 1333 (1*), 1343 (3*), 1355 (3*), 1414 (2), 1443 (10*), 1455 (6*), 1469 (3*), 1633 (9**), 1643 (5**), 1654 (3**), 2101 (1), 2263 (2 b), 2857 (7*), 2872 (4*), 2895 (3 sh*), 2931 (10* b db), 2984 (3*), 3022 (3*), 3089 (3), 3293 (0), 3320-3560 (4, band), 3590 (0), 3602 (3), 3616 (1), 3622 (0). There are residues of the original cis-1-ethynyl-2-methylcyclohexanol; the lines due to these residues are: 2101, 3293, and others).

trans-2-Methyl-1-vinylcyclohexanol (II), $\Delta\nu$ (cm^{-1}): 165 (0), 175 (0), 243 (3*), 257 (3*), 257 (3*), 276 (2*), 287 (3*), 299 (3*), 319 (2), 354 (1), 377 (4), 425 (4), 460 (7), 496 (4*), 511 (4*), 548 (3** b), 567 (3** b), 594 (4** db), 693 (3), 713 (8), 803 (3), 831 (6), 865 (4), 893 (1), 920 (4), 961 (4*), 979 (5*), 997 (6*), 1063 (6), 1082 (1), 1098 (2*), 1113 (2*), 1122 (2*), 1158 (5**), 1184 (3**), 1224 (4), 1264 (6 b), 1298 (6 b), 1349 (5 b), 1409 (5 b), 1436 (8* sh), 1446 (8* sh), 1456 (3* sh), 1468 (3*), 1633 (1), 1644 (9), 1655 (1), 2104 (1), 2659 (1 b), 2852 (8*), 2867 (8*), 2903 (3*), 2921 (10*), 2938 (10*), 2964 (3*), 2982 (2*), 3009 (7), 3089 (3), 3314 (0), 3410-3560 (4 band), 3591 (0), 3601 (1), 3616 (3), 3623 (0). (There are residues of the original trans-1-ethynyl-2-methylcyclohexanol; the lines due to these residues are: 2104, 3314, and others).

cis-2-Methyl-1-vinylcyclohexanol acetate (III) (mixture of trans-ee, trans-aa, and other conformations), $\Delta\nu$ (cm^{-1}): 96 (1), 128 (1), 185 (1), 293 (3), 244 (0), 256 (3), 278 (3), 319 (4), 334 (5*), 342 (5*), 352 (1), 363 (1), 374 (3), 416 (3), 434 (4), 469 (3), 488 (3*), 501 (3*), 510 (3*), 558 (2), 574 (2), 592 (4), 614 (1*), 630 (2), 644 (4*), 653 (3*), 674 (3 db), 704 (3 db), 737 (1), 755 (1), 792 (4*), 803 (4*), 812 (4*), 823 (4*), 859 (7**), 867 (3**), 957 (1 sh), 969 (5*), 980 (5*), 992 (5*), 1002 (7*), 1015 (2*), 1063 (5*), 1093 (4*), 1104 (2*), 1127 (5**), 1151 (5**), 1164 (6**), 1177 (6**), 1194 (0), 1228 (3*), 1270 (7*), 1280 (4*), 1301 (7**),

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*Symbols following intensities: b, broad line; sh, sharp line; db, doublet; the asterisks indicate lines on a background which it has in common with neighboring lines marked with the same number of asterisks.

1313 (7* *), 1348 (3), 1418 (3 b db), 1443 (8*), 1453 (8*), 1463 (3*), 1473 (5*), 1632 (1* *), 1637 (6* *), 1646 (5* *), 1655 (1* *), 1722 (1*), 1734 (3*), 1744 (3*), 1753 (1*), 2100 (1* *), 2113 (3* *), 2126 (1* *), 2858 (6* db), 2899 (1*), 2911 (2* *), 2932 (10*), 2943 (10*), 2956 (4*), 2981 (4*), 3011 (4*), 3025 (3*), 3038 (3*), 3076 (1* *), 3088 (3* *), 3101 (3* *), 3262 (1*), 3283 (1*), 3306 (2*), 3314 (1*). There are residues of ethynyl compounds; the lines due to these residues are: 2100, 2113, 2126, 3262, 3283, 3306, 3314, and others).

trans-2-Methyl-1-vinylcyclohexanol acetate (IV) (mixture of cis-ea, cis-ae, and other conformations) $\Delta \nu$ (cm^{-1}): 89 (6 b), 126 (2), 196 (1), 217 (3*), 229 (3*), 247 (3*), 262 (3*), 274 (3*), 312 (2* *), 340 (1* *), 372 (3*), 380 (3*), 395 (1), 434 (4 db), 465 (6 db), 484 (2), 510 (3 db), 529 (1), 546 (1), 562 (4), 574 (3), 596 (1), 611 (7*), 619 (6*), 628 (5*), 636 (2*), 645 (3*), 654 (3*), 722 (1* *), 737 (4* *), 751 (3* *), 793 (5 db), 832 (6), 860 (5 db), 869 (2), 878 (6), 886 (2), 908 (6), 924 (3 db), 950 (2), 960 (2 sh), 977 (3*), 988 (3*), 999 (7*), 1008 (1*), 1058 (1), 1073 (6 b db), 1114 (1), 1129 (2), 1143 (5 db), 1163 (5*), 1180 (4*), 1212 (1), 1274 (7 b), 1305 (6 b), 1331 (1*), 1344 (2*), 1353 (5*), 1419 (6), 1436 (3* sh), 1444 (8*), 1451 (6*), 1461 (3*), 1470 (2*), 1479 (1* sh), 1630 (1* *), 1637 (6* *), 1645 (5* *), 1724 (1), 1734 (2*), 1743 (4*), 1752 (1), 2103 (1* *), 2113 (5* *), 2122 (1* *), 2772 (3*), 2859 (6* db), 2895 (3*), 2917 (3*), 2930 (10*), 2942 (8*), 2972 (6*), 2984 (6*), 3016 (5*), 3030 (5*), 3081 (4* *), 3094 (6* *), 3102 (1* *), 3271 (0*), 3284 (0*), 3305 (0*), 3314 (1*). (There are residues of ethynyl compounds; the lines due to these residues are: 2103, 2113, 2122, 3271, 3284, 3305, 3314, and others).

cis-1-Ethynyl-2-methylcyclohexanol acetate (V) (mixture of trans-ee, trans-aa, and other conformations), $\Delta \nu$ (cm^{-1}): 85 (2*), 101 (2*), 116 (3* *), 124 (3* *), 134 (3* *), 157 (3*), 172 (2*), 182 (1*), 219 (1* *), 229 (3* * db), 243 (1* *), 253 (3* *), 263 (0), 273 (0), 304 (0), 317 (3* db), 342 (3* db), 375 (3), 390 (0), 413 (3 db), 433 (3), 465 (4), 523 (2), 557 (4* db), 570 (1), 585 (0 sh), 631 (1* sh), 637 (2* sh), 644 (6*), 651 (4*), 722 (3 db), 803 (3), 820 (2*), 836 (2*), 854 (6* sh), 861 (6* sh), 877 (0), 908 (4), 936 (3 db), 962 (1), 984 (4*), 996 (6*), 1006 (3*), 1021 (1), 1044 (0), 1064 (5), 1095 (2), 1127 (6 db), 1171 (6 b db), 1228 (6*), 1237 (2*), 1249 (1*), 1269 (5* *), 1280 (2* *), 1332 (1), 1345 (5*), 1356 (5*), 1443 (8* *), 1451 (8* *), 1459 (4* *), 1473 (2* *), 1721 (1*), 1732 (2*), 1742 (3*), 1754 (1*), 2096 (1* *), 2105 (10* *), 2118 (9* *), 2129 (1* *), 2853 (5* db), 2901 (4*), 2916 (4*), 2931 (10*), 2940 (10*), 2965 (2*), 2979 (3*), 2990 (2*), 3064 (1* *), 3077 (3* *), 3101 (1* *), 3267 (1*), 3286 (1*), 3304 (4*), 3316 (2*).

trans-1-Ethynyl-2-methylcyclohexanol acetate (VI) (mixture of cis-ea, cis-ae, and other conformations), $\Delta \nu$ (cm^{-1}): 89 (1), 118 (1), 129 (1), 136 (0), 159 (0), 177 (0), 207 (0), 220 (3), 233 (1), 243 (1*), 250 (3*), 262 (1*), 312 (1), 332 (2), 372 (2), 396 (4), 449 (0), 465 (4), 485 (2), 510 (1), 572 (4 db), 606 (0), 615 (1*), 624 (7*), 633 (1*), 646 (2), 659 (0), 670 (2), 695 (1), 725 (1), 743 (3 db), 761 (1), 791 (3*), 803 (1*), 821 (1* *), 829 (6* *), 839 (1* *), 865 (2*), 879 (2*), 891 (2*), 908 (5 db), 965 (1), 979 (3*), 993 (1 sh*), 1003 (5*), 1014 (2*), 1045 (3), 1061 (1*), 1077 (3*), 1120 (2), 1141 (1), 1156 (1), 1168 (2*), 1173 (2*), 1235 (2), 1247 (1), 1260 (2), 1273 (6 db), 1322 (1), 1331 (1), 1345 (4* sh), 1360 (4* sh), 1420 (1), 1439 (8*), 1449 (8*), 1456 (3*), 1467 (3*), 1725 (1* *), 1733 (3* *), 1744 (4* *), 1753 (1* *), 2097 (1*), 2107 (10*), 2117 (9*), 2126 (1*), 2851 (6), 2864 (6), 2916 (2*), 2929 (10*), 2914 (10*), 2950 (10*), 2968 (3*), 2986 (3*), 3003 (1*), 3064 (1* *), 3082 (3* *), 3104 (1* *), 3271 (1*), 3289 (1), 3305 (3*), 3317 (1*).

1-Vinylcyclohexanol (VII), $\Delta \nu$ (cm^{-1}): 163 (1), 213 (2*), 231 (2*), 245 (2*), 278 (4* *), 290 (4* *), 299 (2* *), 310 (5* *), 339 (0), 371 (4*), 386 (1*), 425 (4 b db), 478 (1), 490 (1), 516 (4), 537 (0), 558 (0), 571 (2*), 586 (0), 598 (0), 606 (2), 658 (2), 700 (4* db), 717 (4* sh), 727 (9*), 823 (2*), 835 (8* *), 852 (3), 905 (3*), 921 (3*), 940 (4*), 958 (5*), 968 (5*), 1022 (7* *), 1035 (7* *), 1055 (7 sh* *), 1065 (7 sh* *), 1079 (4* *), 1152 (4* db), 1173 (4*), 1185 (4*), 1223 (2), 1269 (9 b db), 1301 (7), 1349 (6), 1405 (6*), 1418 (6*), 1430 (7 sh*), 1438 (10* sh), 1447 (10* sh), 1465 (2*), 1632 (9* *), 1643 (6* *), 2666 (3*), 2681 (2*), 2806 (2* *), 2857 (6* *), 2893 (5* *), 2936 (10* * b), 2981 (1), 3009 (4 b), 3089 (3 b), 3265 (2), 3290–3560 (3, band) 3580 (1*), 3600 (3*), 3615 (2*), 3626 (0*).

1-Vinylcyclohexanol acetate (VIII), $\Delta \nu$ (cm^{-1}): 155 (1), 169 (1), 204 (0), 216 (3*), 226 (4*), 276 (1* *), 287 (5* *), 298 (4* *), 338 (0 sh), 357 (5*), 367 (6*), 377 (5*), 411 (2), 444 (3*), 454 (3*), 473 (3* *), 481 (3* *), 506 (1* sh), 513 (3*), 525 (3*), 532 (3* *), 547 (3* *), 564 (3* *), 579 (2* *), 605 (2*), 614 (6*), 625 (5*), 642 (4*), 654 (1), 667 (6 b db), 714 (0), 726 (0), 736 (6*), 744 (6*), 755 (2*), 770 (2* *), 782 (3* *), 818 (8 sh), 849 (8 sh), 882 (2), 892 (6), 910 (2) 927 (2), 945 (4*), 959 (4*), 1013 (2*), 1034 (9*), 1074 (5 db) 1114 (0), 1134 (5*), 1144 (5*), 1155 (5*), 945 (4*), 959 (4*), 1013 (2*), 1034 (9*), 1074 (5 db), 1114 (0), 1134 (5*), 1144 (5*), 1155 (5*), 1166 (1), 1264 (4* db), 1280 (9* db), 1309 (5), 1328 (0), 1337 (1), 1350 (4 db),

1370 (0), 1415 (7), 1436 (6*), 1449 (10*), 1456 (1*), 1468 (1*), 1634 (9* *), 1644 (8* *), 1652 (1* *), 1723 (1*), 1732 (4*), 1742 (4*), 1750 (1*), 2103 (1* *), 2111 (3* *), 2122 (1* *), 2630 (1), 2653 (2), 2679 (1), 2830 (1*), 2848 (4* sh), 2857 (6*), 2866 (9*), 2894 (4*), 2903 (3*), 2933 (10* sh), 2944 (10* sh), 2977 (4*), 2988 (4*), 3002 (0*), 3017 (8*), 3030 (3*), 3089 (5* *), 3096 (2* *), 3103 (1* *), 3265 (0*), 3286 (0*), 3303 (1*). (There are residues of ethynyl compounds; the lines due to these residues are: 2103, 2111, 2122, 3265, 3286, 3303, 3321, and others).

1-Ethynylcyclohexanol (IX), $\Delta \nu$ (cm^{-1}): 75 (1), 85 (1), 130 (7*), 161 (9* b db), 171(*), 215 (7* * b db), 224 (1* *), 256 (6), 314 (1), 334 (6*), 349 (1*), 381 (5), 431 (5), 459 (5), 526 (4), 539 (0), 555 (4), 613 (6*), 629 (2*), 640 (2*), 650 (2*), 678 (9*), 714 (5), 752 (1), 790 (2), 829 (7*), 837 (2*), 854 (5), 905 (4), 947 (4), 967 (4), 1035 (8), 1061 (7*), 1075 (2*), 1086 (2*), 1139 (3), 1164 (4* db), 1183 (3*), 1264 (7* *), 1279 (3* *) 1317 (2), 1340 (5*), 1352 (5*), 1438 (10* *), 1449 (10* *), 1468 (2* *), 1704 (1), 2100 (10*), 2118 (9*), 2656 (2* *), 2668 (2* *), 2684 (2* *), 2856 (10*), 2864 (10*), 2923 (6*), 2938 (10*), 2956 (10*), 2968 (3*), 3268 (0* *), 3286 (2* *), 3305 (4* *), 3316 (3* *), 3250-3590 (2, band), 3566 (1), 3596 (3), 3611 (2), (1704 = overtone of 854).

1-Ethynylcyclohexanol acetate (X), $\Delta \nu$ (cm^{-1}): 76 (1), 86 (1), 132 (4*), 164 (4*), 176 (2*), 222 (5* *) 254 (3* *), 285 (0), 301 (7), 326 (3 db), 355 (1), 399 (3), 433 (3), 447 (3), 479 (1), 510 (2), 532 (1), 546 (3 db), 566 (5), 637 (6), 668 (8), 686 (0), 705 (0), 715 (1), 727 (3), 746 (3*), 820 (3), 832 (5), 849 (4), 880 (5*), 892 (4*), 917 (1* *), 930 (1* *), 940 (0), 951 (3*), 963 (3*), 1009 (1), 1020 (5*), 1029 (10* sh), 1039 (5*), 1074 (6), 1103 (2*), 1118 (2*), 1133 (2* *), 1144 (2* *), 1155 (2* *), 1202 (12), 1265 (5*), 1279 (5*), 1320 (0), 1349 (4), 1433 (2*), 1448 (8* b), 1468 (1*), 1732 (5* *), 1745 (6* *), 1755 (1* *), 2104 (10*), 2115 (9*), 2124 (3*), 2831 (0), 2851 (5*), 2867 (5*), 2879 (1*), 2926 (3*), 2942 (10*), 2956 (3*), 2986 (3* db), 3263 (1* *), 3282 (1* *), 3303 (3* *), 3316 (2* *).

TABLE 1

Physical Properties of ortho-gem and gem-Substituted Cyclohexanes

Compound No.	Name of compound	B. p. in °C	d^{20}_4	$n^{20}D$	MR	
					found	calc.
I	cis-2-Methyl-1-vinylcyclohexanol	70—71 (9)	0.9398	1.4780	42.17	42.74
II	trans-2-Methyl-1-vinylcyclohexanol	67—68 (10)	0.9318	1.4745	42.26	42.74
III	cis-2-Methyl-1-vinylcyclohexanol acetate	85—86 (12)	0.9786	1.4620	51.12	52.18
IV	trans-2-Methyl-1-vinylcyclohexanol acetate	86—87 (11)	0.9752	1.4605	51.16	52.18
V	cis-1-Ethynyl-2-methylcyclohexanol acetate	88—89 (9)	0.9991	1.4657	49.87	50.39
VI	trans-1-Ethynyl-2-methylcyclohexanol acetate	85 (9)	0.9897	1.4650	50.69	50.39
VII	1-Vinylcyclohexanol	58—59 (8)	0.9890	1.4750	36.02	38.12
VIII	1-Vinylcyclohexanol acetate	71—72 (8)	0.9820	1.4590	48.03	47.37
IX	1-Ethynylcyclohexanol	61—62 (8)	1.0070	1.4810	35.04	36.52
X	1-Ethynylcyclohexanol acetate	79—80 (8)	1.0068	1.4658	45.65	45.77

DISCUSSION OF RESULTS

As we have pointed out in previous papers [1], the pulsating frequency of trans-ortho-substituted cyclohexanes is usually higher than that of the corresponding cis-ortho compounds. Each of the compounds (I) and (II) has two frequencies in the region of the frequencies of the pulsating vibrations of the chair form of the cyclohexane ring, and each of these frequencies has a high intensity in the spectrum of one compound, and a low intensity in the spectrum of the other. The intense frequency is higher [713 (8)] for (II), which indicates that this compound has the trans configuration, whereas (I) with a lower intense frequency [695 (9)], has, accordingly, the cis configuration. The presence of the low-intensity frequencies indicates some admixture of one substance in the other:

(I) cis-2-Methyl-1-vinylcyclohexanol: 695(9), 711(2) cm^{-1}

(II) trans-2-Methyl-1-vinylcyclohexanol: 693(3), 713(8) cm^{-1}

The cis compound may exist in two conformations, ae and ea; and the trans compound may also exist in two conformations, aa and ee (see the scheme at the start of the paper). From general considerations it may be inferred that the energetically favored conformation is that with an equatorial position of the largest substituents in the ring (in the present case, the vinyl and methyl groups). In the cis compound ea is such a conformation, and in the trans compound it is ee. However, factors of various kinds (e.g., the formation of an intermolecular hydrogen bond) may introduce some modifications into this position, and this appears to apply in the present case.

Compounds (I) and (II) form intermolecular hydrogen bonds: this is indicated by the fact that the vibration frequency of the hydroxy group is smeared out into a band and displaced toward the low-frequency end of the spectrum (Fig. 1). On the high-frequency side of this band there are separate lines belonging to the vibration frequencies both of the terminal hydroxyls of associated complexes and of individual molecules that are not hydrogen-bonded. As we have shown [1], the vibration frequency of an equatorial hydroxyl is lower than that of an axial hydroxyl, and under the influence of an intermolecular hydrogen bond the diffuse band of the frequency of an equatorial hydroxyl is displaced further toward the low frequencies than the band of an axial hydroxyl. In the spectra of (I) and (II) the vibration frequency of the hydroxyl in the cis compound (I) is more diffused into a band and is more displaced toward the low frequencies than the corresponding frequency of the trans compound (II): in the spectrum of (I) the band lies approximately in the range 3320-3560 cm^{-1} and its breadth is about 240 cm^{-1}; in the spectrum of (II) the band lies approximately in the range 3410-3560 cm^{-1} and its breadth is about 150 cm^{-1}. The frequency of the most intense line on the high-frequency side of the hydroxyl band is lower (3602 cm^{-1}) for (I) than for (II) (3616 cm^{-1}). In accordance with the above considerations the dominant conformation in (I) is ae with an equatorial position of the hydroxyl, and in (II) it is ee with an axial position of the hydroxyl. The amount of admixed conversion isomers [ea in (I) and aa in (II)] is small if account is taken of the fact that an admixture of (II) in (I) and of (I) in (II) is also manifested in the spectrum of (I) in the feebler frequency 3616 cm^{-1} (epimer ee) and in the spectrum of (II) in the feebler frequency 3601 cm^{-1} (epimer ae):
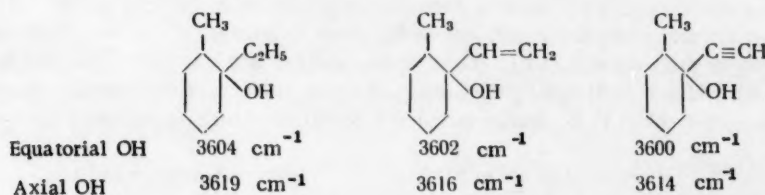
<div style="text-align:center">

Conformation ae in (I)
(equatorial hydroxyl)
3602(3) cm^{-1}

Conformation ea in (I)
(axial hydroxyl)
3616(1) cm^{-1}

Conformation ee in (II)
(axial hydroxyl)
3616(3) cm^{-1}

Conformation aa in (II)
(equatorial hydroxyl)
3601(1) cm^{-1}

</div>

It should be noted that the character of the substitution at the carbon carrying the hydroxyl function enhances the acidic properties of the hydroxyl as we proceed along the series from 1-ethyl- to 1-ethynyl-2-methyl-cyclohexanol, which is manifested in a lowering of the vibration frequency of the hydroxyl [1]:

	CH$_3$—C$_2$H$_5$, OH	CH$_3$—CH=CH$_2$, OH	CH$_3$—C≡CH, OH
Equatorial OH	3604 cm^{-1}	3602 cm^{-1}	3600 cm^{-1}
Axial OH	3619 cm^{-1}	3616 cm^{-1}	3614 cm^{-1}

Chemically, this is manifested in an increase in the rate of acetylation in the same order, and an equatorial hydroxyl (which is the more acid and therefore has a lower vibration frequency) is acetylated more readily than an axial hydroxyl [2]. The regularities observed are in accord with previously published data on the kinetics of the hydrolysis of esters of acetylenic alcohols [3].

Regarding (I) and (II) as substituted ethylenes, we may conclude that the cyclohexane ring belongs to the group of substituents which raise the vibration frequency of the double bond in ethylene; moreover, in the base of an equatorial vinyl group this rise is greater (conformation ee, 1644(9) cm^{-1}) than in the case of an axial vinyl (conformation ae, 1633(9) cm^{-1}). The presence of each of these frequencies at a lower intensity in the spectrum of the other sample [1643(5) in (I) and 1633(1) in (II)] indicates some admixture of one in the other and also the possible presence of a small amount of the conversion isomer ea in (I) and of an extremely small amount of the conversion isomer aa in (II) (Fig. 2).

Conformation ae in (I)
(axial vinyl)
1633(9) cm^{-1}

Conformation ea in (I)
(equatorial vinyl)
1643(5) cm^{-1}

Conformation ee in (II)
(equatorial vinyl)
1644(9) cm^{-1}

Conformation aa in (II)
(axial vinyl)
1633(1) cm^{-1}

It should be noted that in the spectrum of (I) the frequency 711(2) is weakened in intensity to a greater extent than the frequency 1643(5), and in the spectrum of (II), on the other hand, the frequency 1633(1) is weakened in intensity to a greater extent than 693(3). This fact probably indicates that in (I) the nonpredominant conformation appears mainly on account of the conversion ea ⇌ ae, and in (II) mainly on account of admixture of (I).

The spectra of solutions of (I) and (II) in carbon tetrachloride (10% by volume) show that under these conditions the intermolecular hydrogen bonds are broken: the diffuse O−H band in the spectrum disappears, and for practical purposes there remains only one line on the high-frequency side of this band, and this belongs to hydroxyls of monomeric molecules. In the spectrum of the solution of (I) the frequencies 3602 and 1633 cm^{-1} are preserved (3616 and 1643 cm^{-1} are lost in the background), and in the spectrum of the solution of (II) the frequencies 3616 and 1644 cm^{-1} are preserved (3601 and 1633 cm^{-1} are lost in the background). It follows that dissolution in this way, which leads to the rupture of intermolecular hydrogen bonds, does not lead to any substantial conversion of the already-existing dominant conformation ee in (II) (there is no reason why this conversion should occur in view of the considerable energetic favorability of conformation ee, as compared with aa); nor does it lead to any substantial conversion of the dominant conformation ae in (I).

It should be noted that in 1-vinylcyclohexanol (VII) two conformations are possible, ea (−CH=CH$_2$ equatorial, OH axial) and ae (−CH=CH$_2$ axial, OH equatorial).

(VII) ea   (VII) ae
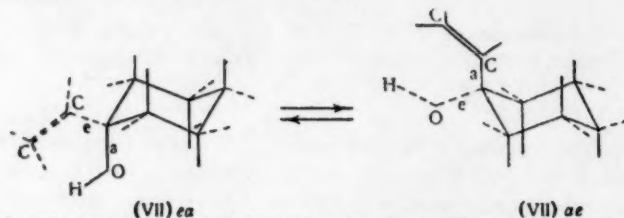
It would appear that, in accordance with Barton's rule, the conformation ea should in this case greatly predominate. However, the pairing of the frequencies of the vibrations of the vinyl group, and also of the hydroxy groups that are not hydrogen-bonded, and the closeness in intensity of the pair of frequencies indicate that both conformations are present in (VII) in considerable amounts and, moreover, the conformation ae is slightly predominant, which is indicated by the somewhat higher intensity of the vibration frequencies of C=C and O−H (not hydrogen-bonded) in the conformation ae, as compared with the conformation ea:

	Conformation ea in (VII) (equatorial vinyl, axial hydroxyl) (cm^{-1})	Conformation ae in (VII) (axial vinyl, equatorial hydroxyl) (cm^{-1})
C=C	1643 (6)	1632 (9)
O−H (not hydrogen-bonded)	3615 (2)	3600 (3)

Some predominance of the conformation ae, in contradiction to Barton's rule, is probably due to the higher strength of the intermolecular hydrogen bond when the hydroxy group has an equatorial position [1]. The bands of the hydrogen-bonded hydroxy groups present in both conformations of (VII) are superimposed in the region 3290-3560 cm^{-1} (Fig. 3).

In the spectra of the acetates (III) and (IV) in the characteristic region of the vibration frequencies of the carbonyl group, there are two relatively intense frequencies at about 1733 and 1743 cm^{-1} and lying on a common background; frequency 1743 cm^{-1} is somewhat more intense than 1733 cm^{-1}. In the region of the frequencies of the ethylenic bond in the spectra of (III) and (IV) there are again, in each case, two frequencies on a common background; these are at about 1637 and 1647 cm^{-1}, and both in (III) and in (IV) the frequency at about 1637 cm^{-1} is somewhat more intense.

In accordance with the above considerations about (I) and (II) (see also [1]), the carbonyl group and ethylenic bond of equatorial substituents have higher vibration frequencies than when these substituents are in the axial position. From this it may be concluded that in the somewhat preferred conformation, both in (III) and in (IV), the substituent $-O-CO-CH_3$ is in the equatorial position and the substituent $-CH=CH_2-$ is in the axial position. What are these conformations?

In the preparation of (III) by the acetylation of cis-1-ethynyl-2-methylcyclohexanol (dominant conformation ae) and subsequent selective hydrogenation of the triple bond to the double bond of (III), the new largest substituent $(O-CO-CH_3)$, which occupies the place of the hydroxyl in the cis-ae conformation of the original substance, now finds itself in the equatorial position. However, we determine the configuration from the mutual positions of the largest substituents, which in (III) are the substituents $-O-CO-CH_3$ and $-CH_3$, which are ortho to one another. Hence, (III) now has to be regarded as a compound having not a cis, but a trans configuration with a dominant conformation of ee. The dominance of ee in (III) corresponds to the Raman-spectrum results and to Barton's rule [1].

In the preparation of (IV) by the acetylation of trans-1-ethynyl-2-methylcyclohexanol (dominant conformation ee) and subsequent selective hydrogenation of the triple bond to the double bond of (IV), the new largest substituent $(-O-CO-CH_3)$, which occupies the place of the hydroxyl in the trans-ee conformation of the original substance, now finds itself in the axial position. According to Barton's rule, this conformation with an axial position of the largest substituent will be unstable and should be converted into the aa conformation if we determine the conformation on the basis of the previous substituents, the vinyl and methyl groups. However, we determine the configuration from the mutual positions of the largest substituents, which in (IV) are the substituents $-O-CO-CH_3$ and CH_3, which are ortho to one another. Hence, (IV) must be regarded as a compound with an ea conformation of cis configuration; the dominance of this configuration in (IV) is in accord with the Raman-spectrum results and to Barton's rule.

As the above spectrum data indicate, in (III) and (IV) the more dominant conformations are accompanied by considerable amounts of others: with an axial position of the $-O-CO-CH_3$ group [frequencies in (III) and (IV) of about 1734 cm^{-1}] and with an equatorial position of the $-CH=CH_2$ group [frequencies in (III) and (IV) of about 1647 cm^{-1}]. The conformations trans-aa and cis-ae can be found both in (III) and in (IV). Why do they appear in this particular case? It should first be noted that in this case the difference in size between the $-CH=CH_2$ and $-O-CO-CH_3$ groups is not sufficiently great (it would be more correct to say that neither particle is sufficiently small in comparison with the other) for Barton's rule to fail; the largest substituent, which is in the axial position because it arises by the acetylation of an axial hydroxyl, is not bound to bring about conversion into an isomer in which the largest substituent has an equatorial position; on the other hand, a largest substituent, which is in the equatorial position because it arises from an equatorial hydroxyl may in the present case by converted into an isomer in which the largest substituent has an axial position because of fluctuations in the conditions under which it exists.

Also, the acetylated starting substances (III) and (IV) do not in either case exist strictly in a single conformation, but contain some of the corresponding epimer and conversion isomers [1]. As a result of all this and of the fact that in this case Barton's rule does not hold strictly, both in (III) and in (IV) the somewhat more predominant conformations are accompanied by the cis-ae and trans-aa conformations:

	Conformation trans-ee in (III) (equatorial $-O-CO-CH_3$, axial $-CH=CH_2$) (cm^{-1})	Conformation trans-aa in (III) (axial $-O-CO-CH_3$, equatorial $-CH=CH_2$) (cm^{-1})
C=O	1744 (3)	1734 (3)
C=C	1637 (6)	1646 (5)

	Conformation cis-ea in (IV) (equatorial $-O-CO-CH_3$, axial $-CH=CH_2$) (cm^{-1})	Conformation cis-ae in (IV) (axial $-O-CO-CH_3$, equatorial $-CH=CH_2$) (cm^{-1})
C=O	1743 (4)	1734 (2)
C=C	1637 (6)	1647 (5)
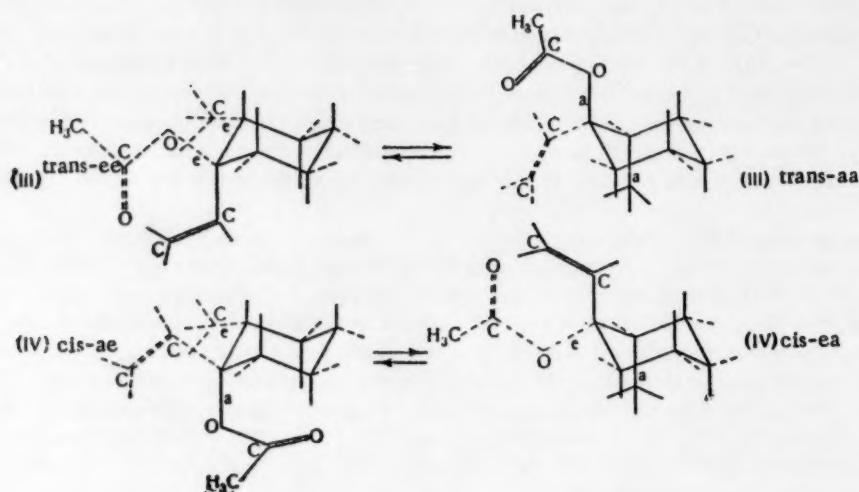
The Raman spectrum of 1-vinylcyclohexanol acetate (VIII) confirms that in this case the difference in the sizes of the substituents ($-HC=CH_2$ and $-O-CO-CH_3$) is not sufficiently great for Barton's rule to be clearly manifest. In this compound, with the cyclohexane ring in the chair form there may be two conformations, ea (equatorial $-O-CO-CH_3$, axial $-CH=CH_2$) and ae (axial $-O-CO-CH_3$, equatorial $-CH=CH_2$):
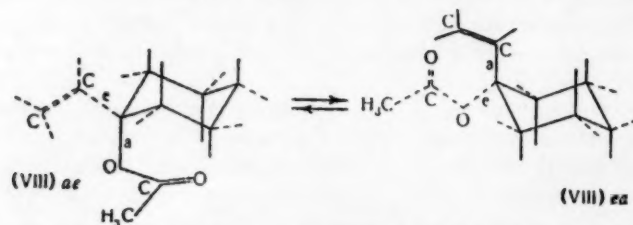
The presence in (VIII) of both these conformations is confirmed by the paired frequencies of C=O and C=C, and also for the pulsating vibration of the ring. These frequencies are almost equal in intensity for both conformations, though some of them are somewhat more intense for the conformation ea, which indicates that this conformation may be slightly more dominant in the present case:

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	Conformation ea in (VIII) (equatorial C=O, axial C=C) (cm^{-1})	Conformation ae in (VIII) (axial C=O, equatorial C=C) (cm^{-1})
C=O	1742 (4)	1732 (4)
C=C	1634 (9)	1644 (8)
Frequency of pulsating vibration of ring	736 (6)	744 (6)

The introduction of an alkyl substituent in the ortho position somewhat favors the formation of a dominant conformation with an equatorial position of $-O-CO-CH_3$, as occurs in (III) and (IV). The above statements about (VIII) confirm the possibility of the above-noted conversions into (III) and (IV).

Acetylation of cis- and trans-1-ethynyl-2-methylcyclohexanols gives the corresponding acetic esters (V) and (VI), and here the phenomena that we have noted in the investigation of (III) and (IV) again occur in relation to the configurations and conformations of (V) and (VI). In this case Barton's rule is again not strictly valid for the analogous conversions because of the insufficiently great difference in the sizes of the gem-substituents in (V) and (VI).

If the configuration is based on the largest substituents (in this case $-O-CO-CH_3$ and $-CH_3$), then it follows from the Raman spectra that in the acetate (V) (prepared from cis-1-ethynyl-2-methylcyclohexanol) the dominant conformation is trans-ee, but there is also a large amount of the conversion isomer trans-aa. In the acetate (VI) (prepared from trans-1-ethynyl-2-methylcyclohexanol) the dominant conformation is cis-ea, but there is also much of the conversion isomer cis-ae:
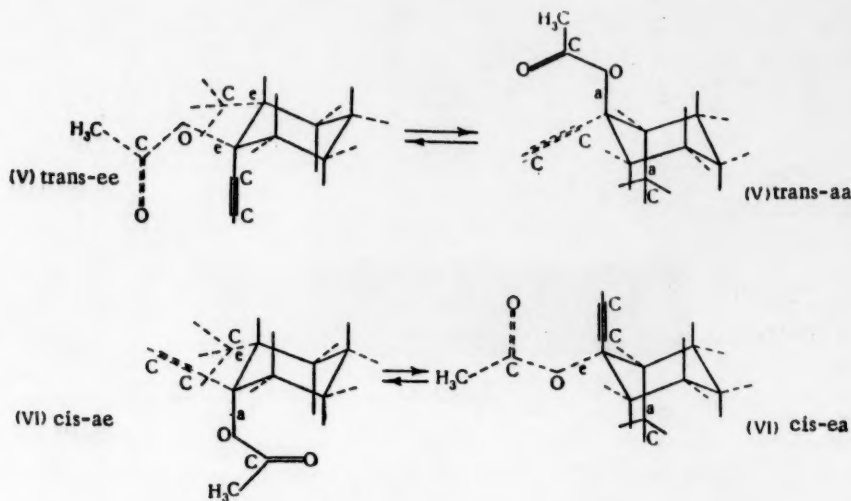
	Conformation trans-ee, in (V) (equatorial $-O-CO-CH_3$, axial $-C \equiv CH$) (cm^{-1})	Conformation trans-aa in (V) (axial $-O-CO-CH_3$, equatorial $-C \equiv CH$) (cm^{-1})
C=O	1742 (3)	1732 (2)
C≡C	2105 (10)	2118 (9)
C−H in ethynyl	3304 (4)	3316 (2)

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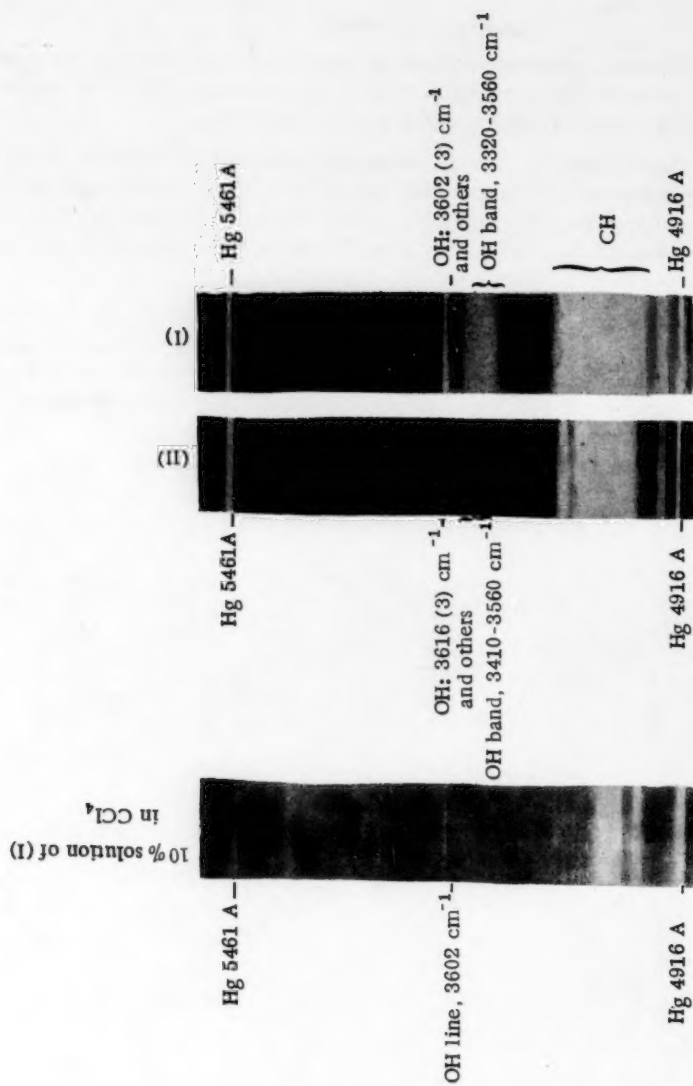
Fig. 1. Raman spectra of cis-2-methyl-1-vinylcyclohexanol (I), trans-2-methyl-1-vinylcyclohexanol (II), and a 10% solution of (I) in CCl₄ in the hydroxyl region.

	Conformation cis-ea in (VI) (equatorial $-O-CO-CH_3$, axial $-C\equiv CH$)	Conformation cis-ae in (VI) (axial $-O-CO-CH_3$, equatorial $-C\equiv CH$)
	(cm^{-1})	(cm^{-1})
$C=O$	1744 (4)	1733 (3)
$C\equiv C$	2107 (10)	2117 (9)
$C-H$ in ethynyl	3305 (3)	3317 (1)

	Conformation ea in (X) (equatorial $C=O$, axial ethynyl)	Conformation ae in (X) (axial $C=O$, equatorial ethynyl)
	(cm^{-1})	(cm^{-1})
$C=O$	1745 (6)	1732 (5)
$C\equiv C$	2104 (10)	2115 (9)
$C-H$ in ethynyl	3303 (3)	3316 (2)

The true proportions of these conformations [as in the case of (III) and (IV)] is somewhat masked by the presence of the corresponding epimers in (V) and (VI) as a result of the admixture of some of one enantiomorph in the other in the original cis- and trans-1-ethynyl-2-methylcyclohexanols (III') and (IV') [1]; after acetylation these admixtures are present in (V) and (VI) in the form of the corresponding epimers.

As in (VII), in the acetylenic alcohol (IX) (see Fig. 3) two conformations are possible: ea, in which the ethynyl substituent occupies an equatorial position and the hydroxyl an axial position, and ae, in which the ethynyl is axial and the hydroxyl equatorial. In (X), as in (VIII), two conformations are again possible: ea with an equatorial $C=O$ and an axial $C\equiv CH$ and ae with an axial $C=O$ and an equatorial $C\equiv CH$. However, in the case of these substances, for the same reasons as in the case of (VII) and (VIII), Barton's rule is not strictly valid: in (IX) the conformation ae is dominant only to a relatively slight extent (beacuse of the stronger inter-molecular hydrogen bond formed by the equatorial hydroxyl), and in (X) the same may be said of the dominance of the conformation ea, as will be seen from the Raman data:

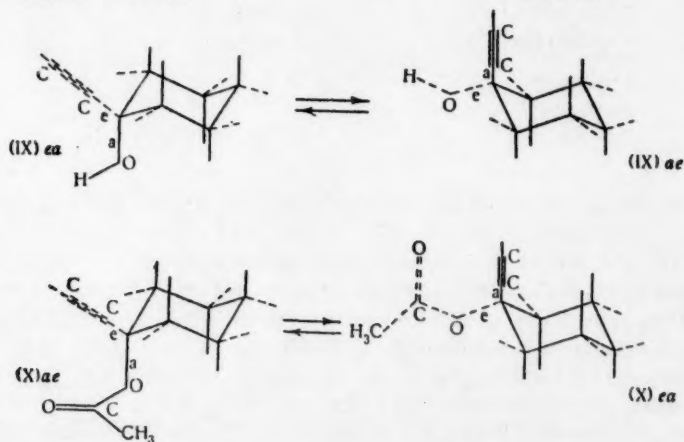|	Conformation ae in (IX) (axial ethynyl, equatorial hydroxyl)	Conformation ea in (IX) (equatorial ethynyl, axial hydroxyl)
	(cm^{-1})	(cm^{-1})
$C\equiv C$	2100 (10)	2118 (9)
$C-H$ in ethynyl	3305 (4)	3316 (3)
$O-H$ (not hydrogen-bonded)	3596 (3)	3611 (2)

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Hg 4916 A

1643 (5)
1633 (9)

Fíg. 2. Raman spectrum of cis-2-methyl-1-vinylcyclohexanol (I) in the double-bond region.

The presence of an alkyl substituent in the ortho position in (V) and (VI) favors [as in (III) and (IV),respectively] some displacement of the conversion equilibrium toward the trans-ee conformation from the trans-aa conformation in (V) and toward the cis-ea conformation from the cis-ae conformation in (VI).

Apart from the intense lines that we have referred to in the text in the regions of the characteristic frequencies of $C=C$, $C=O$, $C\equiv C$, $C-H$ of ethynyl, $O-H$, and other groups in the spectra of the substances investigated, some weak lines, often representing only traces, and also frequencies in the region 820-830 cm^{-1} are observed. It is possible that all these frequencies belong to isomers in which the cyclohexane has the boat form and which are present in the substances investigated in very small amount under the given experimental conditions [1]; rotation isomers are also possible.

As the dominant conformations in the acetates (III) and (IV) (trans-ee and cis-ea) belong to the opposite configurations to the dominant conformations in the original cis- and trans-1-ethynyl-2-methylcyclohexanols (III') and (IV') (see Table 2) when the configuration is determined on the basis of the largest ortho substituents, the Auwers-Skita rule, if it has any physical meaning, must be determined in its application to (III) and (IV) in accordance with their conformations as indicated above, and not in accordance with the original cyclohexanols (III') and (IV'). As compared with the latter, they are, as it were, reversed. This is confirmed (see Table 2) by boiling point data: the cis configuration (IV) has a higher boiling point than the trans configuration (III).

TABLE 2

Substance	Configuration and dominant conformation	B.p. in °C (p in mm)	$n^{20}D$	Original substances for (III), (IV) and (V), (VI)	Configuration and dominant conformation	B. p. in °C (p in mm)	$n^{20}D$
(III)	trans-ee	85-86 (12)	1.4620	(III')	cis-ae (m. p. 56-57°C)	70-75 (6)	—
(IV)	cis-ea	86-87 (11)	1.4605	(IV')	trans-ee	62-65 (6)	1.4780
(V)	trans-ee	88-89 (9)	1.4657				
(VI)	cis-ea	85 (9)	1.4650				

It is necessary to take account of the fact that in this case, for (III) and (IV) as prepared by us, the Auwers-Skita rule is masked by the presence of not only other conformations in these substances, but also of the original substances (III') and (IV') and intermediate products: the Raman spectra show that the acetylation of (III') and (IV') and the subsequent hydrogenation are not carried out to completion [the spectra of (III) and (IV) contain fairly intense frequencies in the region of the characteristic vibration frequencies of the triple and other bonds; see above data on the spectra of these compounds]. If this fact has not invalidated the Auwers-Skita rule in the case of boiling point, then it has masked it in the case of refractive index, which is readily understood in view of the large refraction increment attributable to the triple bond. It may be stated in general that with levelling of the sizes of the ortho substituents, the physical difference between the configurations loses its
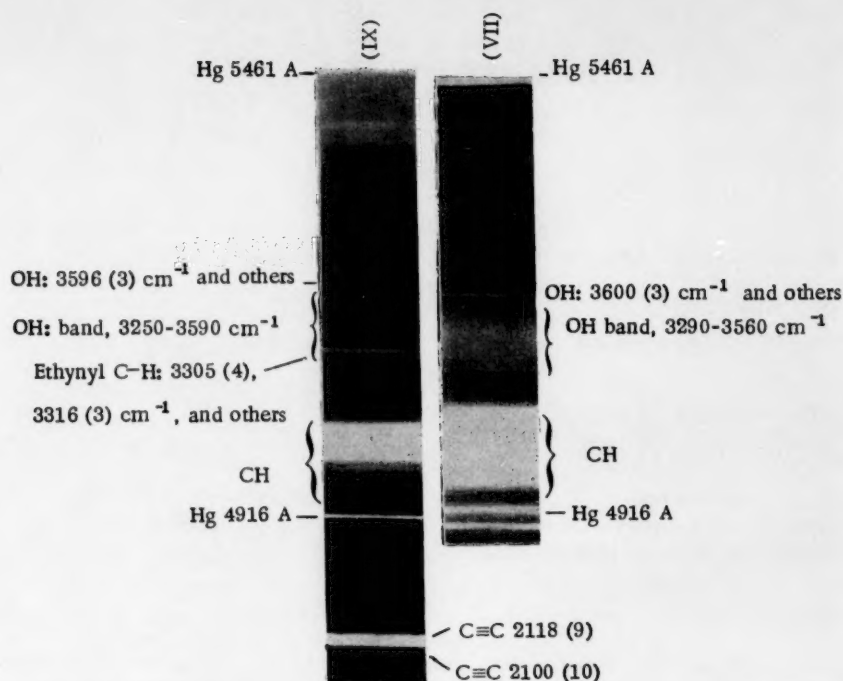
Fig. 3. Raman spectra of 1-vinylcyclohexanol (VII) and 1-ethynylcyclohexanol (IX).

sharpness. As a result, the Auwers-Skita rule loses its precision: the boiling points, refractive indices, and densities of epimers become close in value, and, when there is such a small difference, these properties under the influence of the integrated effect of the factors indicated, may even have reversed values, which is what occurs in the case of (V) and (VI) (Table 2).

SUMMARY

1. Each of the ten gem- and ortho-gem-substituted cyclohexanols investigated exists in the form of a more or less predominant conformation in admixture with conversion and epimeric isomers; the relative amount of the dominant conformation depends on the character of the substituents and other factors, e.g., the presence of an intermolecular hydrogen bond.

2. From its very nature, Barton's rule loses its validity when the relevant substituents do not differ very greatly in size: there is a leveling out of the amounts of conversion isomers in the mixture. In view of all these considerations, the Auwers-Skita rule also ceases to be precise and loses its meaning.

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BRIEF COMMUNCATIONS

ACTION OF COLLAGENASE FROM A CULTURE OF CLOSTRIDIUM HISTOLYTICUM ON SYNTHETIC PEPTIDES DERIVED FROM GLYCINE, L-PROLINE, AND L-HYDROXYPROLINE

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The study of proteins of the collagen group with the aid of collagenase derived from Clostridium histolyticum presents great interest in that this enzyme has an unusually high specificity and will break down only collagen proteins. As the latter have high contents of glycine, L-proline, and L-hydroxyproline, the specific action of collagenase is clearly associated with this fact. In various papers there are indications that collagenase preferentially breaks linkages formed by the amino group of glycine and the carboxy group of L-hydroxyproline [1]. Other authors have succeeded in showing quantitatively that glycine predominates at the amine end and various amino acids at the carboxyl end; arginine and hydroxyproline are present in only very small amounts [2].

Schrohenloher and co-workers [3] showed that in the products of hydrolysis of collagen with collagenase two tripeptides are present in large amount: glycyl-L-proplyl-L-hydroxyproline and glycyl-L-prolyl-L-alanine, which contain about 63% of imino acids, 23% of alanine, and 14% of glycine. Schroeder and co-workers [4], on the basis of the hydrolysis of collagen, proposed the possible alternation of -gly-pro-hydroxypro-gly- as the structural unit of the molecule.*

Grassman and co-workers [4] isolated an interesting fragment rich in glycine, proline, and hydroxyproline, which, from the point of view of the quantitative proportions of amino acids, may correspond to the above-cited proposal of Schroeder. In this connection work on the synthesis of possible substrates for collagenase is of interest. Heyns and Legler [5] have referred to the synthesis of two substrates: the amide of (benzyloxycarbonyl)alanyl-glycyl-proline and the amide of (benzyloxy)prolyl-alanyl-glycyl-proline. Nagai and Noda [6] reported on the hydrolysis of poly(prolyl-leucyl-glycine) and the amide of glycyl-prolyl-leucylproline with collagenase. However, all these contain other amino acids apart from glycine and imino acids. We considered that it would very interesting to verify the action of collagenase on peptides of the type isolated by Grassmann [4] and Schroeder [3], i.e., containing only glycine, L-proline, and L-hydroxyproline. For this purpose we synthesized the peptides themselves and some derivatives (see table). The methods of synthesizing and characterizing the compounds will be given in the next communication. In the hydrolysis we used collagenase which had no nonspecific proteolytic activity; this was determined by the splitting of native and heat-denatured albumin from horse serum, hemoglobin, and casein [1]. The activity of the resulting collagenase preparation was measured by the rate of fall of the viscosity of procollagen solutions [1]. The activity of the enzyme was tested also on synthetic amide of (benzyloxycarbonyl)-DL-alanyl-glycyl-L-proline. It was found that the methyl ester of (benzyloxycarbonyl)-DL-alanyl-glycyl-L-proline was not hydrolyzed by the collagenase.

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* The references to Literature Cited are given as in the original; it should be noted that the numbers given in the text often do not correspond with those given in Literature Cited, and the reference to Nagai and Noda does not appear in Literature Cited. — Publisher.

TABLE

No.	Compound [*]	Hydrolyzability of peptide with collagenase	Rf
1	BZC-DL-alanyl-glycyl-L-prolyl-NH$_2$	+	0.27; 0.56; 0.92
2	BZC-DL-alanyl-glycyl-L-prolyl-OCH$_3$	−	
3	BZC-L-prolyl-DL-alanyl-glycyl-L-prolyl-OCH$_3$	+	0.49; 0.92
4	BZC-L-prolyl -glycyl-glycyl-L-prolyl-OCH$_3$	−	
5	BZC-L-prolyl -glycyl-glycyl-glycyl-L-prolyl-OCH$_3$	+	0.55; 0.87
6	BZC-L-prolyl-glycyl-glycyl-L-prolyl-L-hydroxyprolyl-OCH$_3$	−	
7	BZC-glycyl-L- prolyl-L-hyroxyprolyl-glycyl-glycyl-L-prolyl-OCH$_3$	+	0.43; 0.53; 0.76
8	BZC-L-prolyl-glycyl-glycyl-L-hydroxyprolyl-OCH$_3$	−	
9	BZC-glycyl-L-prolyl-prolyl-glycyl-L-prolyl-L-prolyl-OCH$_3$	−	
10	Glycyl-L-prolyl-L-prolyl-glycyl-L-prolyl-L-prolyl-OCH$_3$	−	
11	BZC-glycyl-L-prolyl-L-hydroxyprolyl-glycyl-L-prolyl-L-hydroxyprolyl-OCH$_3$	+	0.38; 0.82
12	Glycyl-L-prolyl-L-hydroxyprolyl-glycyl-L-prolyl-L-hydroxyprolyl-OCH$_3$	+	0.18; 0.35
13	BZC-glycyl-L-prolyl-L-prolyl-glycyl-OCH$_3$	−	
14	BZC-L-prolyl-glycyl-L-prolyl-glycyl-OCH$_3$ [8]	−	
15	BZC-glycyl-L-prolyl-glycyl-L-hydroxyprolyl-OCH$_3$	−	
16	Glycyl-L-prolyl-glycyl-L-hydroxyproline	−	
17	L-Prolyl-glycyl-L-proline [7]	−	
18	L-Prolyl-glycyl-L-hydroxyproline [8]	−	
19	Glycyl-L-prolyl-L-hydroxyproline [7]	−	
20	Glycyl-L-prolyl-glycine [7]	−	
21	Glycyl-L-prolyl-L-proline [7]	−	

[*] BZC) C$_6$H$_5$CH$_2$OCO; +) peptide is hydrolyzed by collagenase; −) peptide is not hydrolyzed by collagenase.

To determine the part played by the amide group we synthesized the methyl ester of (benzyloxycarbonyl)-L-propyl-DL-alanyl-glycyl-L-proline, which was hydrolyzed by collagenase. It may be concluded that the amide group may not play a determining part in peptides containing four or more amino acid residues. In the table we have compounds (4), (5), (6), (7), and (8), which contain two and three glycine residues between two prolines (or hydroxyproline and proline); compounds (9), (10), (11), (12), and (13), which contain the alternating tripeptide glycyl-L-prolyl-X (X is L-proline or L-hydroxyproline); compounds (14), (15), and (16), which contain simple alternations of L-proline and glycine; and compounds (17) − (21), which are tripeptides containing glycine and an imino acid. From our point of view great interest is centered in compounds (7), (11), and (12), which contain elements of natural fragments. It was found that all these compounds are hydrolyzed by collagenase to different extents. However, replacement of L-hydroxyproline by L-proline [compounds (9) and (10)] makes them stable to the action of the enzyme. At present we are drawing no conclusions regarding the specificity of collagenase, but will state only that the collagenase from Clostridium histolyticum can clearly be used for the splitting of peptides consisting exclusively of glycine and imino acids. It is interesting that the presence of three glycine residues between two prolines in a compound renders it capable of being split by the enzyme, whereas a simple alternation of prolyl-proline or glycyl-proline makes these compounds stable to the action of the enzyme. It may be found that regions of collagen saturated in glycine and imino acids may include fragments in which the residues are in such an order that the fragments are inaccessible to the action of collagenase. In this respect, the enzyme proliniminopeptidase, which can split polyproline [5], may be of interest.

EXPERIMENTAL

The enzyme was used in a buffer solution containing 3% of CaCl$_2$ and having pH 7.2. The required pH was attained by addition of Ca(OH)$_2$ to the CaCl$_2$ solution. To determine the fermentative action of the

collagenase on the peptide or peptide derivative, 3-4 mg of the latter was mixed with 30-50 γ of the enzyme preparation and dissolved in 0.3-0.5 ml of the buffer; the mixture was then thermostated at 37° for 12 hours (as a control, the substance under test was kept in the buffer under the same conditions). The hydrolysis products were identified by paper chromatography in 4:5:1 butyl alcohol — water — acetic acid on "Leningrad Type B" paper. The chromatograms were developed both with tolidine and with isatin. In the chromatography of the hydrolyzate of the amide of (benzyloxycarbonyl)-DL-alanyl-glycyl-L-proline we detected three products with corresponding spots with R_f 0.27, R_f 0.56, and R_f 0.92, the second of these being very weak. The spot with R_f 0.27 was eluted from the paper with 10 ml of hot water, the solution was evaporated, and the residue was hydrolyzed with 6 N HCl in a boiling water bath for six hours. On chromatography of the hydrolyzate and development with isatin we identified glycine and proline from the R_f of the spots and their colors. From this we may conclude that collagenase splits off the amide of glycine-L-proline. The spot with R_f 0.56 may be the result of the cyclization of the amide of glycyl-L-proline into the anhydride of glycyl-L-proline. The spot with R_f 0.92 is an unseparated mixture of (benzyloxycarbonyl)alanine and the original substrate.

In an analogous way we hydrolyzed the methyl esters of (benzyloxycarbonyl)glycyl-L-prolyl-L-hydroxy-prolyl-glycyl-L-prolyl-L-hydroxyproline, (benzyloxycarbonyl)-L-prolyl-glycyl-glycyl-glycyl-L-proline, (benzyloxycarbonyl)glycyl-L-prolyl-L-hydroxyprolyl-glycyl-glycyl-L-proline, (benzyloxycarbonyl)-L-prolyl-DL-alanyl-glycyl-L-proline, and glycyl-L-prolyl-L-hydroxyprolyl-glycyl-L-proline-L-hydroxyproline itself. The kinetics of the hydrolysis and the identification of the hydrolysis products obtained with collagenase will be described in a future communication.

In conclusion the authors thank the direction of the Institute of Medicinal and Biological Chemistry of the Academy of Medical Sciences, V. N. Orekhovich, and G. A. Levdikova for the presentation of collagenase.

SUMMARY

1. The methyl esters of synthetic (benzyloxycarbonyl)glycyl-L-prolyl-L-hydroxyprolyl-glycyl-L-prolyl-L-hydroxyproline, (benzyloxycarbonyl)glycyl-L-prolyl-L-hydroxyprolyl-glycyl-glycyl-L-proline, (benzyloxy-carbonyl)-L-prolyl-glycyl-glycyl-glycyl-L-proline, and (benzyloxycarbonyl)-L-prolyl-DL-alanyl-glycyl-L-proline were found to act as substrates for collagenase.

2. Collagenase may be used also for the hydrolysis of peptides containing only glycine and imino acids.

3. Peptides consisting of alternations of glycylproline or prolylproline are stable to the action of collagenase.

4. In principle, the replacement of an amide group by an ester group in peptides containing four or more amino acid residues has no effect on the substrate activity of the peptides.

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*Original Russian pagination. See C. B. Translation.

RESOLUTION OF RACEMIC HYDROCARBONS INTO THEIR ANTIPODES

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The ability of urea to form clathrate compounds which crystallize preferentially in the form of one of the crystalline enantiomorphs has been applied recently in the resolution of various racemic compounds into their antipodes; the compounds that have been resolved include halogen derivatives of normal hydrocarbons and esters [1]. The preferential separation of one optical isomer in a clathrate compound is brought about by the introduction of a seed crystal or the use of optically active solvents [2]. This method is of particular interest for the resolution of racemic compounds that do not contain functional groups, e.g., hydrocarbons. The detection of optical activity in a hydrocarbon isolated as a clathrate compound facilitates the investigation of the composition of, and extent to which branching occurs in petroleum hydrocarbons, because urea can form clathrate compounds only with those hydrocarbons which have a normal structure or only methyl side groups. The hydrocarbons obtained from urea clathrate compounds in the usual treatment of petroleum fractions have no optical activity; it is necessary to introduce a seed crystal of the clathrate compound of the optically active hydrocarbon to effect partial resolution of the racemate.

For this investigation we synthesized racemic and optically active 3-methyloctane and 3-methylnonane. The starting material was optically active 2-methyl-1-butanol of 85% optical purity. Optically active 3-methyloctane was prepared by the Wurtz reaction from optically active 1-iodo-2-methylbutane (α^{20}D + 2.0°) and butyl iodide. When bromides are used in this reaction, and also when the preparation is effected via the organomagnesium compound, optically inactive hydrocarbons are obtained. The resulting 3-methyloctane had b. p. 143-144° (755 mm) and $[\alpha]^{20}$D + 4.93° (α^{20}D + 1.52° ± 0.03; l = 1.9009; c = 16.2 in isooctane), which corresponds to 52.5% optical purity.

For the preparation of the homologous optically active 3-methylnonane we used the method for hydrocarbon synthesis by the hydrogenolysis of thiophene compounds [3] by the scheme:
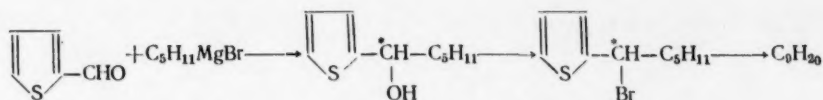
In the synthesis of the hydrocarbon the intermediate optically active alcohol and bromo compound were obtained for the first time. α-2-Methylbutyl)-2-thiophenemethanol, which was obtained in 70% yield, had b. p. 255-260° (755 mm), 20° (10 mm); n^{15}D 1.5480; d^{15}_4 1.0629; MR 54.98; $[\alpha]^{23}$D + 10.04° (α^{23}D + 2.39° ± 0.03; l = 1.9009; c = 12.5 in ether).

The thiophenemethanol was converted into the bromo compound by the action of 47% HBr. This gave 2-(1-bromo-3-methylpentyl)thiophene; b. p. 160-170° (40 mm), 83-90° (18 mm); n^{20}D 1.5380; d^{20}_4 1.2204; MR 63.3 $[\alpha]^{20}$D + 2.2° (α^{20}D + 0.6° ± 0.03; l = 1.9009; c = 14 in ether). The hydrogenolysis of the bromo compound was effected by boiling it with ten times the amount of freshly prepared Raney nickel in CCl$_4$ solution.

The hydrogenolysis appeared to be accompanied by partial racemization of the optically active compound. We obtained 3-methylnonane having $\alpha^{20}D = +0.18° \pm 0.005$; ($l = 1.9009$); b. p. 167.5°; d^{20}_4 0.7350; $n^{20}D$ 1.4120.

The resolution of racemic hydrocarbons into their antipodes was carried out as follows. An eightfold amount of a solution of urea in absolute methanol (saturated at 20°) was added to a solution of optically active 3-methyloctane in isooctane; a crystalline clathrate compound was obtained.

Crystals of the clathrate compound (0.1 g) were washed with isooctane and added to a petroleum fraction of b. p. 141-147.5° and containing 3-methyloctane. By the application of heat the crystals were brought into solution, and the whole remained optically inactive (0.00 ± 0.003°) within the limits of experimental error. An eightfold amount of urea solution was added to the solution. Slow crystallization over a period of 20 hours with constant lowering of temperature from 45° to 10° led to the separation of a crystalline clathrate compound. The precipitate was washed with isooctane, decomposed with water, and extracted with benzene. The hydrocarbons isolated from the precipitate had $\alpha^{20}D - 0.9074° \pm 0.003$ ($l = 1.9009$); the hydrocarbon obtained from the filtrate had $\alpha^{20}D$ 0.055° ± 0.003 ($l = 1.9009$, benzene). The hydrocarbon isolated from the precipitate corresponded in constants to 3-methyloctane.

Another part of the crystalline clathrate compound containing optically active hydrocarbon was added to synthetic racemic 3-methyloctane. The hydrocarbon isolated from the precipitate in an analogous way had $\alpha^{20}D - 0.061°$ ($l = 1.9009$, benzene). By the action of crystals of the clathrate compound containing optically active 3-methylnonane on the 141-147.5° fraction, hydrocarbons were obtained from the precipitate and filtrate having, respectively, $\alpha^{20}D - 0.007° \pm 0.003$ and $+0.126° \pm 0.003$ ($l = 1.9009$, benzene). The results permit us to suppose that, when crystals of the clathrate compound containing optically active 3-methyloctane are introduced as "seeds," there probably arises a partial dynamic equilibrium in the clathrate compound between the optically active hydrocarbon in the inner space of the clathrate compound and the same racemic hydrocarbon in the medium. As a result, the number of crystallization centers bringing about optically selective crystallization is reduced. In the case of the clathrate compound containing 3-methylnonane, such displacement of optically active molecules from the clathrate compound by molecules of the medium does not occur or occurs to a small extent. Consequently, the resolution of the racemate brought about by such a seed crystal is found to be more effective.

SUMMARY

1. Partial resolution of racemic hydrocarbons into their antipodes was effected by introduction of seed crystals of a clathrate compound of the optically active hydrocarbon.

2. Optically active hydrocarbons and two thiophene compounds were synthesized.

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SYNTHESIS OF ETHERS OF FERROCENEMETHANOL

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We have previously described [1, 2] the preparation of the phenyl and 2-naphthyl ethers of ferrocenemethanol and also the preparation of 1-(ferrocenylmethoxy)-4-(phenylazo)benzene from the methiodide of (dimethylaminomethyl)ferrocene.

In the present work we synthesized the methyl, ethyl, t-butyl, nonyl, decyl, allyl, benzyl, and furyl ethers of ferrocenemethanol from the methiodide or ethobromide of (dimethylaminomethyl)ferrocene [N,N-dimethyl-ferrocenemethylamine].

$$C_5H_5FeC_5H_4CH_2N(CH_3)_3 \, I \xrightarrow[\text{(NaOH)}]{\text{ROH}} C_5H_5FeC_5H_4CH_2OR$$
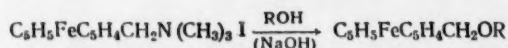
The reaction was carried out in the usual way for the alkylation of alcohols with quaternary ammonium salts [3-5] by heating the latter in excess of the alcohol in presence of sodium hydroxide (apart from the nonyl and decyl ethers). Yields of 60-80% were obtained, except in the case of the t-butyl ether, which was formed in a yield of only 9%; in addition we obtained appreciable amounts of the bisferrocenylmethyl ether $(C_5H_5FeC_5H_4CH_2)_2O$, and more than 30% of the original methiodide was recovered unchanged.

Taking the benzyl ether of ferrocenemethanol as our example, we showed that the possible rearrangement under the action of alkali of the methiodide of (dimethylaminomethyl)ferrocene [6] does not occur under the conditions of the preparation: the benzyl ether of ferrocenemethanol was synthesized without addition of alkali and also from benzyl alcohol and ferrocenemethanol in presence of diboron trioxide, and the ethers obtained in all three cases were found to be identical.

The nonyl and decyl ethers of ferrocenemethanol were prepared by heating the ethobromide of (dimethyl-aminomethyl)ferrocene with nonyl and decyl alcohols, respectively, without addition of alkali; yields 28-30%.

EXPERIMENTAL

Methyl ether of ferrocenemethanol $C_5H_5FeC_5H_4CH_2OCH_3$. A solution of 6 g (0.0156 mole) of the methiodide of (dimethylaminomethyl)ferrocene and 6 g (0.150 mole) of sodium hydroxide (analytical quality) in 100 ml of absolute methanol was heated with exclusion of moisture for 12 hours in a boiling water bath. The mixture was then poured into cold water (500 ml), and the methyl ether of ferrocenemethanol was extracted with petroleum ether (4 portions, each 75-100 ml). The solution was washed with water, with 2% HCl solution, and again with water until it was neutral to litmus; it was then dried. Solvent was vacuum-distilled off, and the residual methyl ether was distilled: b. p. 118.5-119.5° (3 mm); $n^{20}D$ 1.5996; yield 3.0 g (83%). Found: C 62.41; 62.61; H 6.45; 6.32; Fe 23.90; 23.85%. $C_{12}H_{14}FeO$. Calculated: C 62.63; H 6.14; Fe 24.27%.

Ethyl ether of ferrocenemethanol $C_5H_5FeC_5H_4CH_2OC_2H_5$. This was prepared by the above-described procedure, but the time of heating was increased to 16 hours. Yield 63%; b. p. 117-118° (3 mm); $n^{20}D$ 1.5850. Found: C 63.57; 63.60; H 6.61; 6.57; Fe 22.53; 22.69. $C_{13}H_{16}FeO$. Calculated: C 63.95; H 6.61; Fe 22.87%.

t-Butyl ether of Ferrocenemethanol $C_5H_5FeC_5H_4CH_2OC(CH_3)_3$. A mixture of 1.5 g (0.0039 mole) of the methiodide of (dimethylaminomethyl)ferrocene, 1.5 g (0.0375 mole) of sodium hydroxide, and 40 ml of absolute t-butyl alcohol was heated in a water bath without access of moisture for 14 hours. The mixture was then poured into 250 ml of petroleum ether, the solution was filtered, and the precipitate was washed three times on the filter with 20 ml portions of hot petroleum ether.

The precipitate was then dissolved in methanol, the solution was neutralized with a little concentrated hydrochloric acid, the precipitated sodium chloride was filtered off, and unchanged methiodide was precipitated with ether; weight 0.5 g (33% of original amount); decomposition temperature 205-207° (from alcohol); mixture with original substance had decomposition temperature 206-208°.

The solution in petroleum ether was washed with water, with 10% HCl solution, and again with water; it was dried with calcium chloride. Part of the solvent was distilled off (to a volume of 100 ml), and the reaction products were separated chromatographically on alumina. The first to be eluted with a 10:1 mixture of petroleum ether and diethyl ether was the t-butyl ether of ferrocenemethanol; yield 0.1 g (9.4%); m. p. 73.5-74° (from petroleum ether). Found: C 66.37; 66.22; H 7.60; 7.67; Fe 20.16; 20.38. $C_{15}H_{20}FeO$. Calculated: C 66.18; H 7.42; Fe 20.51%.

We further separated 0.1 g of a red oily substance which contained no iron and was insoluble in methanol; its structure was not investigated.

The last to be eluted (with a 1:1 mixture of petroleum ether and diethyl ether) was bisferrocenylmethyl ether; yield 0.2 g (25%); the melting point, alone and in admixture with a known sample, was 129.5-130°.

When the t-butyl alcohol contained water, the main reaction product was ferrocenemethanol (yield 12%); not even traces of the t-butyl ether of ferrocenemethanol were then isolated.

Ethobromide of (dimethylaminomethyl)ferrocene $C_5H_5FeC_5H_4CH_2N(CH_3)_2C_2H_5Br$. A mixture of 21.8 g of ethyl bromide and 30 ml of dry ether was added to a solution of 24.3 g of (dimethylaminomethyl)ferrocene in 30 ml of benzene. After some time there was a precipitate of the ethobromide of (dimethylaminomethyl)ferrocene, which was filtered off, dissolved in chloroform, and then precipitated with ether; yield 25.3 g (95%); decomp. temp. 160-163° (in a sealed capillary). Found: C 51.05; 50.84; H 6.75; 6.67; Br 22.66; 22.46; N 3.97; 4.14%. $C_{15}H_{22}FeNBr$. Calculated: C 15.16; H 6.31; Br 22.70; N 3.97.

Nonyl ether of ferrocenemethanol $C_5H_5FeC_5H_4CH_2OC_9H_{19}$. A mixture of 1.5 g of the ethobromide of (dimethylaminomethyl)ferrocene and 2.5 ml of nonyl alcohol was heated for eight hours at 80-100°. The reaction mixture was then extracted with petroleum ether; the solution was washed with water, dried, and subjected to chromatography on alumina. The yield of the nonyl ether of ferrocenemethanol was 0.5 g (28%); m. p. 22.5-23.5° (from methanol). Found: C 69.92; 69.99; H 9.05; 8.85; Fe 16.23; 16.37%. $C_{20}H_{30}FeO$. Calculated: C 70.20; H 8.83; Fe 16.32%.

Decyl ether of ferrocenemethanol $C_5H_5FeC_5H_4CH_2OC_{10}H_{21}$. This was synthesized like the nonyl ether; yield 30%; m. p. 35-37° (from methanol). Found: C 70.54; 70.61; H 9.30; 9.19; Fe 15.86; 15.75%. $C_{21}H_{32}FeO$. Calculated: C 70.76; H 9.07; Fe 15.67%.

Allyl ether of ferrocenemethanol $C_5H_5FeC_5H_4CH_2OCHCH_2 = CH_2$. This was prepared like the methyl ether; yield 60%; b. p. 120-121° (2.5 mm); $n^{20}D$ 1.5908. Found: C 65.64; 65.46; H 6.15; 6.26; Fe 21.05; 20.93%. $C_{14}H_{16}FeO$. Calculated: C 65.64; H 6.30; Fe 21.80%.

Benzyl ether of ferrocenemethanol $C_5H_5FeC_5H_4CH_2OCH_2C_6H_5$. This was prepared like the methyl ether and purified by chromatography on alumina. Yield 80%; m. p. 88-89° (from petroleum ether). Found: C 70.55; 70.81; H 5.87; 5.98; Fe 17.87; 17.99%. $C_{18}H_{18}FeO$. Calculated: C 70.59; H 5.93; Fe 18.23%.

The benzyl ether of ferrocenemethanol, identical with the above-described product, was obtained also by carrying out the reaction without the addition of NaOH (yield 55%) and by the reaction of ferrocenemethanol with benzyl alcohol in presence of diboron trioxide.*

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* These two syntheses were carried out by A. A. Ponomarenko.

When 1 g of ferrocenemethanol, 10 ml of benzyl alcohol, and 0.5 g of diboron trioxide were heated together for ten hours at the boil, 1.1 g (75%) of the benzyl ether was obtained.

Furyl ether of ferrocenemethanol $C_5H_5FeC_5H_4CH_2OC_5H_5O$. This was prepared like the methyl ether, but its solution in petroleum ether was not washed with dilute hydrochloric acid. Yield 58%; m. p. 49.5-50.5° (from petroleum ether). By chromatography of the mother liquor on silica gel, a further small amount of the product was obtained. When kept over acidic drying agents, the furyl ether resinified. Found: C 65.27; 65.08; H 5.74; 5.62; Fe 18.21; 18.48%. $C_{16}H_{18}FeO$. Calculated: C 64.88; H 5.45; Fe 18.85%.

SUMMARY

1. The previously undescribed methyl, ethyl, t-butyl, nonyl, decyl, allyl, benzyl, and furyl ethers of ferrocenemethanol were prepared by the action of the alcohols with the methiodide or ethobromide of (dimethyl-aminomethyl)ferrocene.

2. No rearrangement of the methiodide occurs under the action of sodium hydroxide under the conditions for the preparation of ethers of ferrocenemethanol.

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RAMAN-SPECTRUM INVESTIGATION OF 2-BUTYNE-1,4-DIOL

2-BUTYNE-1,4-DIOL DIACETATE, AND 1,4-DICHLORO-2-BUTYNE

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In the Raman spectrum of 2-butyne-1,4-diol a rather rare phenomenon is found: an unusually noteworthy Raleigh wing covering the spectrum range of approximately 0-350 cm^{-1} and merging at the end with the lines 312-343 cm^{-1}. A similar Raleigh wing is observed in the spectrum of liquid formic acid; in this it characterizes the intermolecular vibrations through hydrogen bonds by which the formic acid molecules are associated into complexes [1]. It is clear that in butynediol the usual breadth of the band in the region of the wing of the Raleigh line is due to intermolecular vibrations in complexes formed through hydrogen bonds. These complexes are extremely stable, for butynediol is insoluble in such neutral solvents as CCl_4. Both hydroxyls of each molecule take part in the hydrogen-bonding of butynediol. These complexes may be cyclic or linear, as can be seen from the diagram:
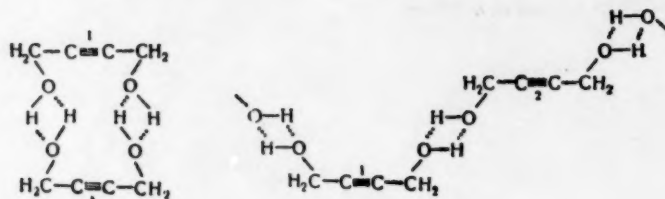
The position of the band due to the valence vibration of a hydrogen-bonded hydroxyl, which generally lies above 300 cm^{-1}, cannot be located exactly because of the considerable background observed in this part of the butynediol spectrum.

In the complexes of butynediol molecules, hydrogen-bonded hydroxyls may occupy cisoid (numbered 1 in the diagram) and transoid (numbered 2 in the diagram) positions in cyclic (trimers, etc.) and linear complexes, and this probably results in the presence of the pair of frequencies (doublet) in the triple-bond region of the butynediol spectrum.* The hydrogen bonds stabilize these isomeric forms. All the bonds of the small molecule

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* The appearance of a doublet in the region of the frequencies of $C \equiv C$ vibrations in disubstituted acetylenes is customarily explained, since the appearance of the paper [2], as due to Fermi resonance of the fundamental frequency of the $C \equiv C$ vibrations with the octave of a fundamental tone in the region of 1100 cm^{-1}, which is forbidden in the Raman spectrum. This explanation, however, cannot be of general significance. With regard to this argument, Kohlrausch [3] states: "It is quite unlikely that in systems such as
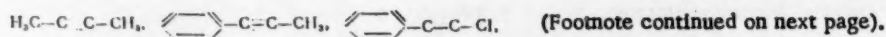
of butynediol in the liquid phase of this substance will be substantially affected by the vibrations of the inter-molecular hydrogen bonds. This effect is transmitted to the vibrations of the bonds through frequency modulation of their intermolecular vibrations, as a result of which, for example, instead of two frequencies for the vibrations of the $C-H$ bonds of the methylene group, two bands are observed in the spectrum, the first of breadth about 30 cm^{-1}, and the second of breadth about 65 cm^{-1}; each of them consists of a set of frequencies (see below, spectrum region 2853-2963 cm^{-1}). The vibrations of the $C-O$ and $C-C$ bonds (in the region 966-1042 cm^{-1}) are also represented by a set of frequencies; each of the two frequencies of the $C \equiv C$ bond is a doublet, etc.

In compounds with open chains containing multiple bonds and C-halogen bonds, these bonds, as the experimental data show, tend to arrange themselves in one plane; their diamagnetic susceptibility is greatest in the direction perpendicular to this plane [4]. With a flat arrangement of these bonds, in butynediol diacetate and in 1,4-dichlorobutyne cisoid and transoid forms are possible, as can be seen from the following examples:
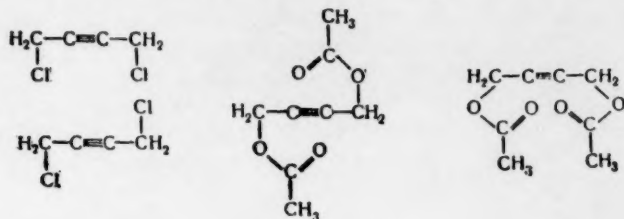
Consequently, in the spectrum of 1,4-dichlorobutyne there are two triple-bond frequencies (2240, 2330 cm^{-1}), two $C-Cl$ frequencies (695, 705 cm^{-1}), two $C-C$ frequencies (1160, 1172 cm^{-1}), etc.; in the spectrum of butynediol diacetate there are two (triplet) $C \equiv C$ frequencies, two (doublet) $C=O$ frequencies, etc. In the spectrum of 1,4-dichlorobutyne no transformation of a line into a set of frequencies is observed in the way found in the spectrum of butynediol because in 1,4-dichlorobutyne the intermolecular actions are not as strong as in 1,4-butynediol. Thus, the methylene groups in 1,4-dichlorobutyne are represented only by the two frequencies of their symmetrical and antisymmetrical vibrations (2950, 2991), etc.; the doubling of the frequencies of the $C \equiv C$, $C-Cl$, and $C-C$ bonds can be completely explained by the presence of the two isomers of 1,4-dichlorobutyne indicated. However, in the diacetic ester molecule, both in the transoid and in the cisoid forms, there is a field interaction of the carbonyl group and the electron envelope of its oxygen atom with the unscreened side of the positive nuclei of the carbon atoms of the triple bond [4], so that the $C \equiv C$ frequencies both of the transoid and of the cisoid form break up into triplets (2231, 2243, 2257 and 2298, 2313, 2328 cm^{-1}) and the carbonyl group in each of the forms is represented by two frequencies (1743 and 1729; 1754 and another coinciding with 1743 cm^{-1} or lost in its background).

EXPERIMENTAL

We give here the main physical properties of the compounds investigated [5]:

	B. p. (°C) / p (mm)	M. p. (°C)	$n^{20}D$
2-Butyne-1,4-diol	$\dfrac{147-148}{16}$	57-58	–
1,4-Dichloro-2-butyne	$\dfrac{68-69}{22}$	–	1.5040
2-Butyne-1,4-diol diacetate	$\dfrac{117-118}{8.5}$	28	1.4540

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of which the first has high symmetry and the last low, there would be equally high and equally unobservable fundamental tones at about 1100 cm^{-1} which would give rise to Fermi resonance. In any case, this fundamental tone is not observed in the Raman spectra; almost all of the spectra cited have no frequencies in the 1100 cm^{-1} region."

The Raman spectra of these substances were determined in the liquid phase on a Soviet ISP-51 spectrograph with a central camera and on a Hilger E-612 spectrograph; the exciting radiation was the 4358 A blue line from a mercury lamp (for symbols accompanying intensities see [6]).

Butynediol $\Delta \nu$ (cm^{-1}): ~ 0-350, wing of Raleigh line, 312 (2*), 320 (3*), 333 (3*), 343 (3*), 463 (1), 491 (1), 589 (1), 695 (1), 966 (1*) − 988 (1*) − 1005 (1*) − 1017 (3*) − 1028 (3*) − 1042 (2*) band, 1129 (1), 1231 (2), 1357 (3), 1445 (3*), 1459 (3*), 2203 (5**), 2216 (5**), 2272 (6*), 2285 (6*), 2853 (3**) − 2868 (5**) − 2883 (3**) band, 2900 (2*) − 2914 (3*) − 2929 (5*) − 2939 (3*) − 2949 (2*) − 2963 (1*) band (the frequencies of OH vibrations in the region above 3000 cm^{-1} were not determined because of the background).

1,4-Dichlorobutyne, $\Delta \nu$ (cm^{-1}): 251 (2*), 266 (2*), 278 (1*), 310 (2**), 324 (3**), 334 (3**), 417 (1*), 430 (2*), 442 (3*), 455 (3*), 695 (10**), 705 (10**), 785 (6), 903 (3 sh), 1160 (3*), 1172 (3*), 1190 (0), 1207 (4), 1267 (9), 1429 (6), 2240 (10), 2330 (4), 2419 (1) [overtone of 1207 (2)], 2950 (10), 2991 (6).

Butynediol acetate, $\Delta \nu$ (cm^{-1}): 172 (1), 186 (1), 255 (1), 273 (2*), 286 (3*), 298 (1*), 329 (3*), 337 (6*), 345 (6*), 368 (5**), 385 (5**), 413 (3 b), 448 (0 b), 490 (4*), 502 (4*), 515 (4*), 542 (2**), 551 (1**), 566 (2**), 603 (3*), 630 (6* db), 647 (1*), 668 (3*), 770 (0), 804 (5), 836 (7 db), 847 (1), 916 (6*), 929 (6*), 968 (4**), 978 (4**), 1023 (5* sh), 1033 (9* sh), 1042 (5 sh*), 1217 (3**), 1229 (3**), 1240 (3**), 1257 (1), 1278 (3 db), 1300 (0), 1318 (0), 1333 (0), 1362 (9*), 1381 (6*), 1435 (7**), 1454 (6**), 1729 (1*), 1743 (5*), 1754 (5*), 2231 (5 sh**), 2243 (10 db**), 2257 (5**), 2298 (4*), 2313 (5*), 2328 (2*), 2933 (10*), 2946 (6*), 2957 (2*), 2971 (2*), 2990 (2*), 3003 (2*), 3025 (1*).

SUMMARY

2-Butyne-1,4-diol, 2-butyne-1,4-diol diacetate, and 1,4-dichloro-2-butyne exist in cisoid and transoid forms because of the operation of factors hindering free rotation of individual groups of atoms in these molecules around the corresponding single bonds.

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STRUCTURAL PECULIARITIES OF SOME SINGLE BONDS IN SYSTEMS CONTAINING MULTIPLE BONDS

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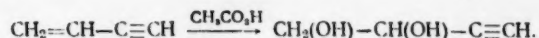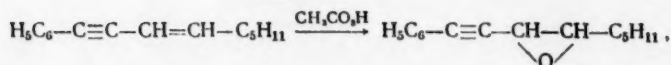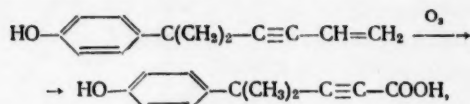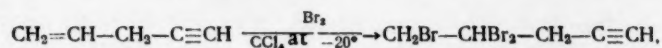No. 3, pp. 558-560, March, 1960
Original article submitted July 17, 1959

Investigations carried out during the last decade have established the following about compounds containing multiple bonds: 1) a considerable shortening of a single C—C bond that is adjacent to a triple bond (to about 1.47 A in propyne) or between two multiple bonds (to about 1.36 A in butadiyne), as compared with its length in ethane, taken as standard (1.55 A) [1]; 2) the absence of free rotation around single C—C bonds in conjugated systems and the consequent presence in them of isomers of the cisoid and transoid types [2]:

$$\diagup\diagdown\diagup \, , \; \diagup\diagup\diagdown \, ; \; \diagup\!=\!\diagup \, , \; \diagup\!=\!\diagdown \, , \text{etc.}$$
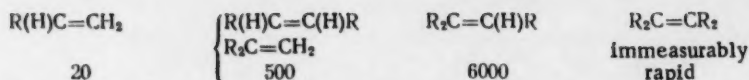
The elucidation of these peculiarities in the structures of compounds containing multiple bonds is greatly helped by an examination of the specific reactivity of the acetylenic bond and the determination of the factors on which it depends.

In comparison with a double bond, a triple bond is less reactive toward electrophilic reagents (halogens, ozone, peroxy acids) and more reactive toward nucleophilic reagents (alcohols, amines, arylamines, ammonia, water) [3-6]. Thus, when bromine is added in a deficient amount to a mixture of acetylenic and ethylenic compounds, there is almost selective attack on the latter [7]. When electrophilic bromine, ozone, or a peroxy acid reacts with a compound containing both a double and a triple bond, reaction proceeds selectively at the double bond with formation of primary products in which the triple bond remains intact [3, 7]:

$$CH_2\!=\!CH\!-\!CH_2\!-\!C\!\equiv\!CH \xrightarrow[\text{CCl}_4 \text{ at } -20°]{Br_2} CH_2Br\!-\!CHBr_2\!-\!CH_2\!-\!C\!\equiv\!CH,$$

$$HO\!-\!\langle\bigcirc\rangle\!-\!C(CH_3)_2\!-\!C\!\equiv\!C\!-\!CH\!=\!CH_2 \xrightarrow{O_3}$$

$$\rightarrow HO\!-\!\langle\bigcirc\rangle\!-\!C(CH_3)_2\!-\!C\!\equiv\!C\!-\!COOH,$$

$$H_5C_6\!-\!C\!\equiv\!C\!-\!CH\!=\!CH\!-\!C_5H_{11} \xrightarrow{CH_3CO_3H} H_5C_6\!-\!C\!\equiv\!C\!-\!\underset{\diagdown O \diagup}{CH\!-\!CH}\!-\!C_5H_{11},$$

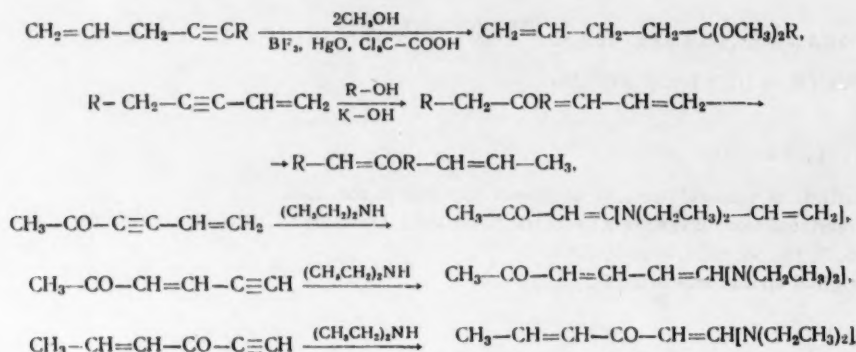$$CH_2\!=\!CH\!-\!C\!\equiv\!CH \xrightarrow{CH_3CO_3H} CH_2(OH)\!-\!CH(OH)\!-\!C\!\equiv\!CH.$$

The very much greater rate of reaction of electrophilic peroxy acids with the ethylenic bond than with the acetylenic bond is seen from the following data (R is alkyl, and the rate of reaction with ethylene is taken as unity) [3]:

$HC\equiv CH$	$RC\equiv CH$	$RC\equiv CR$	$H_2C\!=\!CH_2$
extremely slow	0.1	0.5	1

$$R(H)C=CH_2 \qquad \begin{cases} R(H)C=C(H)R \\ R_2C=CH_2 \end{cases} \qquad R_2C=C(H)R \qquad R_2C=CR_2$$

$$\text{20} \qquad\qquad\qquad \text{500} \qquad\qquad \text{6000} \qquad \begin{array}{c}\text{immeasurably}\\ \text{rapid}\end{array}$$

On the other hand, the reactions of analogous compounds with nucleophilic reagents proceeds at the triple bond; in the primary addition product the double bond remains unaffected [3, 8]:

$$CH_2=CH-CH_2-C\equiv CR \xrightarrow[BF_3, \ HgO, \ Cl_3C-COOH]{2CH_3OH} CH_2=CH-CH_2-CH_2-C(OCH_3)_2R,$$

$$R-CH_2-C\equiv C-CH=CH_2 \xrightarrow[K-OH]{R-OH} R-CH_2-COR=CH-CH=CH_2 \longrightarrow$$

$$\longrightarrow R-CH=COR-CH=CH-CH_3.$$

$$CH_3-CO-C\equiv C-CH=CH_2 \xrightarrow{(CH_3CH_2)_2NH} CH_3-CO-CH=C[N(CH_2CH_3)_2-CH=CH_2],$$

$$CH_3-CO-CH=CH-C\equiv CH \xrightarrow{(CH_3CH_2)_2NH} CH_3-CO-CH=CH-CH=CH[N(CH_2CH_3)_2].$$

$$CH_3-CH=CH-CO-C\equiv CH \xrightarrow{(CH_3CH_2)_2NH} CH_3-CH=CH-CO-CH=CH[N(CH_2CH_3)_2]$$

It should be noted that the additions both of halogens [6] and of hydrogen halides [9] to an acetylenic bond are now beginning to be treated as nucleophilic addition reactions.

The first ionization potential of the triple $C \equiv C$ bond is 21 kcal/mole (9%) greater than that of an ethylenic bond [10]. Hence, reactions starting with electrophilic attack should proceed at an acetylenic bond considerably less preferentially than is observed in practice. However, in itself this factor still does not explain the high tendency for the acetylenic bond to react with nucleophilic reagents, the reason for which is revealed in the following.

In compounds of the type CR_4, in which the $C-R$ bonds have the tetrahedral angles, the positive nucleus of the carbon atom is most uniformly screened by its electron envelope (approximately symmetric distribution of the octet of electrons). The carbon atom of an ethylenic bond is attached to three atoms by three bonds which usually lie in one plane and form angles with one another of about 120°; when two pairs of electrons are concentrated in the double bond, the positive charge of the carbon atom of the ethylenic bond is to some extent exposed on both sides of the plane. An acetylenic carbon atom is attached to two atoms by one single and one triple bond, which are arranged linearly at an angle of about 180°. With the concentration of three pairs of electrons in the triple bond, the carbon atom is greatly exposed on the side of the single bond; the electron envelope of an acetylenic carbon atom is extremely asymmetric; each of the two atoms of an acetylenic bond is highly polarized: $-\overset{+-}{C} \equiv \overset{-+}{C} -$. The effect of the positive field of the exposed side of the nucleus of a carbon atom of an acetylenic bond is to render the bond particularly prone to attack by nucleophilic reagents and also to influence the structures of bonds adjacent to the acetylenic bond: the electron system of the neighboring atom is attracted, and with it the atom itself as a result of the "struggle" for electrons; consequently, the length $\underline{r}$ of the neighboring single bond is reduced [1 and others]:

TABLE

Compound	Bond	r(A)	Compound	Bond	r(A)
Ethane	$H-C(H_2)-$	1.102	Hexamethylethane	H_3C-C-	1.54
Ethylene	$H-C(H)=$	1.071	Methylacetylene	$H_3C-C=$	1.47
Acetylene	$H-C\equiv$	1.058	Dimethylacetylene	$H_3C-C\equiv$	1.47
Hexachloroethane	$Cl-C$	1.77	Hexabromoethane	$Br-C$	1.93
Tetrachloroethylene	$Cl-C$	1.71	Tetrabromoethylene	$Br-C$	1.91
Dichloroacetylene	$Cl-C$	1.64	Dibromoacetylene	$Br-C$	1.80

TABLE (continued)

Compound	Bond	r (A)
Ethane	C−C	1.55
Butadiene	=C−C=	1.48
Butadiyne	≡C−C≡	1.36

This discussion still does not provide an explanation for the free rotation around central single C−C bonds in conjugated systems; this peculiar feature arises mainly by the interaction of local magnetic fields. Polyatomic organic molecules are usually diamagnetic, i.e., have no magnetic moment of their own, are magnetically neutral. This magnetic neutrality is due to the interaction of paired spin and paired orbital magnetic moments, and this interaction to a large extent determines both the valence link, mainly on account of paired spins, and also the mutual orientation of individual groups of atoms in the molecule, mainly on account of orienting interaction between orbital magnetic moments.

The experimental data show [11] that in aliphatic compounds containing multiple bonds the latter tend to arrange themselves in one plane and the diamagnetic susceptibility is greatest in the direction perpendicular to this plane. It appears [11] that, when multiple bonds are present in the molecule, forces arise which compel some of the electrons of these bonds to occupy orbitals lying in one plane. This arises mainly from the orienting interaction (pairing) of orbital magnetic moments, and with the pairing of spins this results in magnetically neutral planes, magnetically neutral layers in the molecule, magnetic neutrality of the molecule as a whole, and also the arrangement of the multiple bonds in one plane. The magnetic neutrality of molecules containing conjugated bands is equally ensured in both plane cisoid and plane transoid forms. The potential barrier separating them is low (e.g., 2.3 kcal/mole in 1,3-butadiene), and the more stable form, which has the lower energy, is the transoid form [2].

SUMMARY

1. The experimentally established considerable shortening of a single C−C bond situated next to a triple bond (propyne, etc.) or between two multiple bonds (butadiyne, etc.) is due mainly to the asymmetry of the electron envelopes of carbon atoms forming the multiple bonds; the asymmetry leads to considerable polarization of these atoms.

2. The experimentally established absence of free rotation around single C−C bonds in conjugated systems (butadiene, etc.) and the consequent occurrence of cisoid and transoid isomers arise from the interaction of the orbital magnetic moments of the electrons of the conjugated multiple bonds.

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ROLE OF A THIRD PARTICLE IN THE REACTION BETWEEN O AND CO

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In the previous investigation [1] we measured the effective rate constant for the elementary reaction between atomic oxygen and molecular carbon monoxide, which we presented in the form:

$$k = 3 \cdot 10^{-15} \sqrt{T} \cdot e^{-\frac{3000}{RT}} \ \text{cm}^3 \cdot \text{sec}^{-1}$$

Our conclusion that the reaction had a bimolecular reaction was based on experiments at constant pressure. It was of interest to check and add further precision to these conclusions by experiments in which the concentration of a third particle is not kept constant. In the present work the procedure and apparatus were the same as before [1], but a different reaction vessel was used in which, unlike the previous one, the surface was coated with potassium chloride. Experiments were carried out at two pressures (2.5 and 14.5 mm). Results of the measurements of relative concentrations of atomic oxygen along the length of the vessel are presented in Fig. 1. The origin of the coordinates is an obligatory point. The results in Fig. 1 were obtained at 428°K. In accordance with considerations given previously [1], the existence of proportionality between the quantities represented on the graph indicates a predominance of linear decay of oxygen atoms over quadratic decay. From Fig. 1 we obtained the rate constants for linear decay k_0 for two pressures. The calculation was carried out according to the formula: $k_0 = 2.3 \cdot w \cdot \tan \gamma$ (w is the linear velocity of the stream; γ is the angular slope of the straight line in Fig. 1). For a pressure of 2.5 mm, $k_0 = 66 \, \text{sec}^{-1}$; for a pressure of 14.5 mm, $k_0 = 102.5 \, \text{sec}^{-1}$.
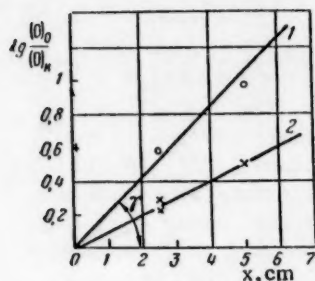
Fig. 1. 1) Pressure 2.5 mm; 2) pressure 14.5 mm.

Figure 2 shows the results of measurements of the final concentrations $(CO_2)_k$ as a function of the initial concentration $(CO)_0$. From the data in Fig. 2 we obtained the effective rate constants for the reaction $O + CO \rightarrow CO_2$ for two pressures. Calculations of rate constants were carried out from the formula:

$$k = k_1 + k_2 (M) = \frac{bk_0}{\text{tg} \, \alpha}$$

The values of b and tan α were obtained from Fig. 2. For 2.5 mm, $k = 2.4 \cdot 10^{-15}$, and for 14.5 mm, $k = 3 \cdot 10^{-5}$ $\text{cm}^3 \cdot \text{sec}^{-1} \cdot \text{molecule}^{-1}$. As will be seen from the figures cited, the effective rate constant for reaction between O atoms and CO depends only slightly on pressure over the range of pressures measured.

A clearer treatment of the experimental result is obtained if an examination is made of the structure of the effective constant $\underline{k}$ which we measured experimentally. Consider the following scheme for the mechanism of this reaction:

$$O + CO \underset{+M}{\overset{+M}{\rightleftarrows}} \begin{cases} CO_2^* & k_1 \\ CO_2 + M & k_2 \\ CO_2^{**} + M & k_3 \end{cases}$$

$$CO_2^* \overset{+M}{\longrightarrow} \begin{cases} CO + O & k_4 \\ CO_2 + h\nu & k_5 \\ CO_2 + M & k_6 \\ CO_2^{**} + \Delta h\nu & k_7 \end{cases}$$

$$CO_2^{**} \overset{+M}{\longrightarrow} \begin{cases} CO_2 + h\nu & k_8 \\ CO_2 + M & k_9 \end{cases}$$

$$O + O + M \longrightarrow O_2 + M \qquad k_0^m$$

$$O + M \longrightarrow \text{termination} \qquad k_0^n$$
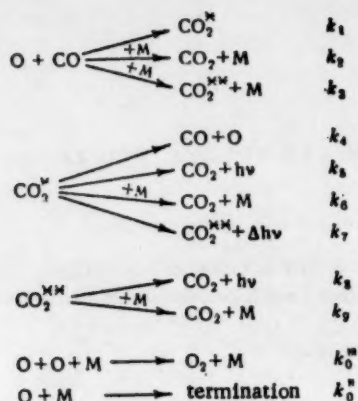
In this scheme CO_2^* is an unstable complex, and CO_2^* is a complex which is stabilized, but is in an activated state.

Fig. 2. 1) Pressure 2.5 mm; 2) pressure 14.5 mm.

From this scheme, starting from the condition for a stationary state

$$\frac{d\,CO_2^*}{dt} = 0$$

we may obtain an expression for the effective constant in the form

$$k = (k_2 + k_3)\,M + k_1\,\frac{k_5 + (k_6 + k_7)\,M}{k_4 + k_5 + (k_6 + k_7)\,M}. \qquad (1)$$

The absence of any appreciable dependence of $\underline{k}$ on M over the range measured indicates that in Eq. (1) the magnitude of $(k_2 + k_3)M$ can be neglected over the given range of pressures. Also, the absence of any dependence on pressure indicates that in Eq. (1) the second term is approximately equal to k_1 over the given pressure range. Equation (1), therefore, may be written in the form:

$$k \approx k_1$$

Hence, the experimental data and the scheme for the mechanism of reaction between O and CO indicates a predominance of bimolecular processes over termolecular processes in the pressure range under consideration. Hence, our measured effective rate constant $\underline{k}$ is actually the constant of the bimolecular process k_1. The experimental data obtained allow us also to estimate the upper limit of the sum of constants $k_2 + k_3$ of the ternary collisions of the reaction

$$O + CO + M \overset{k_2}{\longrightarrow} CO_2 + M$$

$$O + CO + M \overset{k_3}{\longrightarrow} CO_2^{**} + M$$

from the fact that in our measurements of $\underline{k}$ we observed only a slight rise of $\underline{k}$ with pressure lying within the limits of experimental error; we may write the inequality:

$$(k_2 + k_3)\, M < 0.6 \cdot 10^{-15} \ cm^3 \cdot sec^{-1} \cdot molecule^{-1}$$

Substituting the value of M at 428°K and 14.5 mm ($3.3 \cdot 10^{17}$), we obtain:

$$(k_2 + k_3) < 2 \cdot 10^{-33} \ cm^6 \cdot sec^{-1} \cdot molecule^{-1}$$

The experimental data obtained therefore confirm the conclusion reached by us earlier [1] concerning the bimolecular mechanism of this reaction at pressures up to 10 mm.

The question of the mechanism of this reaction at higher pressures also becomes clearer. Thus, on the basis of our results it may be shown that under the conditions of the carbon monoxide flame at atmospheric pressure and 2000°K there will be a predominance of the bimolecular mechanism for reaction between O atoms and CO. In fact, calculating the effective constant from our formula:

$$k = 3 \cdot 10^{-15} \sqrt{T} \cdot e^{-\frac{3600}{RT}} \ cm^3 \cdot sec^{-1} \cdot mole^{-1}$$

for T = 2000° we obtain $k = 6.4 \cdot 10^{-14} cm^3 \cdot sec^{-1}$, whereas the product $(k_2 + k_3)M$, which determines the rate of the termolecular process at 2000° and 760 mm, has a maximum of $7.5 \cdot 10^{-15} \cdot cm^3 \cdot sec^{-1}$. A comparison of the effective reaction rates and the rate of the termolecular process shows clearly the predominance of the bimolecular process. This conclusion is in close accord with the conclusion of Zel'dovich and Semenov [2]. On the basis of a comparison of experiment with theory, for the rate of burning of CO these authors concluded that a bimolecular mechanism for the reaction $O + CO \longrightarrow CO_2$ is in better accord with experiment than a termolecular mechanism.

Under conditions of low temperature and high pressure the predominance of the termolecular mechanism cannot be excluded, but this is not obviously so, and further investigation is required.

SUMMARY

1. The rate constant for reaction between O and CO at various pressures was measured.

2. The reaction $O + CO \longrightarrow CO_2$ is bimolecular over a wide range of temperature and pressure.

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*Original Russian pagination. See C. B. Translation.

DETERMINATION OF THE ENERGY OF THE BOND FORMED BY CARBON
WITH THE SURFACE OF A NICKEL CATALYST

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The energy of the bond formed by carbon with the surface of a nickel catalyst was estimated by Balandin [1] from a comparison of the relative readiness with which various reactions of complex organic compounds occur, and it was calculated by us [2, 3] from kinetic data. For its thermodynamic evaluation we shall consider equilibrium in the reaction

$$x[K] + A = [K]_x A. \tag{1}$$
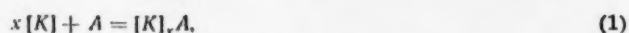
in which A is an atom of the reactant, which reacts through $\underline{n}$ valences with $\underline{x}$ atoms of [K], the catalyst surface.

The bond energy $Q_{A-[K]}$ will be understood as the heat of reaction (1), $-\Delta H'$, referred to one valence of A, i.e.,

$$Q_{A-[K]} = -\frac{1}{n}\Delta H'. \tag{2}$$

In this we regard the atoms [K] as not in the free state, as is generally done in calculations of the energies of the rupture of bonds [4, 5], but, in accordance with the calculations carried out previously, as a component of a catalyst surface having free valences. If reaction (1) is applied to one [K] atom, i.e.,

$$[K] + 1/x \, A = [K] A_{1/x}, \tag{3}$$

we may write

$$Q_{A-[K]} = -\frac{x}{n}\Delta H. \tag{4}$$

in which $-\Delta H$ is the heat of reaction (3).

For analogous reaction with K atoms, which enter into the bulk phase of the crystal lattice of the catalyst

$$K + 1/x^* \, A = K A_{1/x^*}. \tag{5}$$

we have

$$Q^*_{A-K} \qquad \frac{x^*}{n}\Delta H^*. \tag{6}$$

in which all quantities refer to the bulk phase of the catalyst. From Eq. (4) and (6) we obtain

$$Q_{A-[K]} = \frac{x^*}{x} Q_{A-K}^{\cdot} - \frac{x}{n} (\Delta H - \Delta H^*). \tag{7}$$

In the papers [6-8] it is assumed that as we pass from the bulk-phase compound to the corresponding surface compound the entropy changes so little that the change in its value can be neglected. This assumption follows from the applicability of the Nernst heat law to adsorption phenomena [9] and is justified by the results obtained. In particular, this assumption was made for the surface compounds formed by oxygen with a nickel catalyst. In the present case, it follows from an analogous assumption that

$$\Delta H - \Delta H^* \approx \Delta F - \Delta F^* \tag{8}$$

[ΔF and ΔF^* are free energy changes in reactions (3) and (5)], whence

$$Q_{A-[K]} = \frac{x}{x^*} Q_{A-K}^{\cdot} - \frac{x}{n} (\Delta F - \Delta F^*). \tag{9}$$

Unlike ΔH^* and ΔF^*, the values of ΔH and ΔF may vary at different sites on the surface or with different coverage of the surface. As shown in [6], for a uniformly heterogeneous surface the value of the entropy term does not change at medium coverages of the surface; at low and high coverages it is necessary to make a correction for the "configuration term" of the entropy, the value of which is given in [8]. Hence, for the values of ΔH and ΔF we may take their average values for the given surface or consider them for individual sites of different degrees of coverage. As the values of $Q_{A-K}^{\cdot}$ can be calculated from tabulated values for the corresponding bulk compound, the question of finding $Q_{A-[K]}$ amounts to the determination of the excess of energy of the surface compound $[K]A_{1/x}$.

We shall assume that the excess of free energy ($\Delta F - \Delta F^*$) is determined mainly by the excess of free energy of surface atoms of catalyst, the free valences of which saturate the valences of A. This assumption, which is a natural one, permits the use of Eq. (9) for finding values of $Q_{A-[K]}$ for various surface compounds of the given catalyst with A, A', A", etc., if the value of the excess of free energy is known for one of these surface compounds.

Using these assumptions, let us examine the equilibrium

$$[N_i] + 1/x\, C_{(gas)} = [N_i]\, C_{1/x}. \tag{10}$$
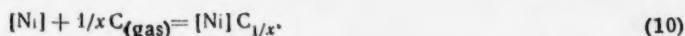
For the bulk phase of nickel the available data apply to the reaction

$$Ni_{(s)} + 1/x^* C_{(s)} = N_i C_{1/x^*(s)} \tag{11}$$

the enthalpy change in which may be calculated (as in [10]) from the equilibrium

$$N_i C_{1/x^*} + 2/x^* H_2 = Ni + 1/x^* CH_4. \tag{12}$$

From the data in [10] the value of $- \Delta H$ for reaction (11) is $(7.4/x^*)$ kcal/mole (in range 350-650°), and from the data in [11] in the range 226-285°, $- \Delta H$ is $5.0/3 - 6.5/3$ kcal/mole. From calorimetric data obtained from heats of combustion, $- \Delta H = - 9.2/3$ kcal/mole [12].

In this case we shall regard the data in [10] as the most reliable. As the data given above refer to solid carbon, for our calculations we shall take account of the transition

$$C_{(s)} = C_{(g)} \tag{13}$$
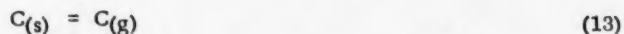
According to the latest review by Kondrat'ev [5], the heat of atomization of carbon is 171.3 kcal/g-atom. According to our data [7, 8], the value of ($\Delta F - \Delta F^*$) for the equilibrium [Ni] + $\frac{1}{2}$ O_2 = [Ni]O on a nickel catalyst which does not contain promotors or carrier and has a uniformly heterogeneous surface varies from 1.6 to 4.2 kcal/mole; the average value of ($\Delta F - \Delta F^*$) for x = 1 and n = 2 is 2.9 kcal/mole, or 1.45 kcal/mole per valence.

The composition of bulk nickel carbide corresponds to $x^* = 3$. The composition of the surface compound [Ni]$C_{1/x}$ may vary with the coverage from x = ∞ to x = 1 (covalent radius of carbon = 0.71-0.75 A; the area occupied by a nickel atom on the densest faces (111) and (100), which are most frequently found on the surface is on the average equal to $5.74 \cdot 10^{-16}$ sq.cm). For medium coverages $\underline{x}$ is close to the value 2. Hence, in accordance with Eq. (9), the correction for the excess of free energy is 2.9 kcal/mole for x = 2, but if x = 4 (at lower coverages) it will be 6 kcal/mole.

In this way, from our data on the excess of free energy and the data in [10] and [11] on the equilibrium (12), with the aid of Eq. (9) and neglecting the temperature dependence of ΔH we obtain a bond energy $Q_{C-[Ni]}$ of 26.6-26.9 kcal/mole for medium coverages of a nickel catalyst. The values are close to those calculated by us earlier from kinetic data for the energy of the bond formed by a nickel catalyst with carbon occurring in a compound in a position adjacent to a double bond [2, 3]. This value, recalculated with introduction of the newly accepted heat of atomization of carbon [5], is 28.1 kcal/mole [13].

In an analogous way, for complete coverage of the surface we obtain $Q_{C-[Ni]}$ = 14.0-14.1 kcal/mole, which is close to the value of the energy calculated from kinetic data for a bond with carbon occurring in a compound in a position adjacent to a single bond [3, 13].

It should be noted that Eq. (9) holds when A enters into a more complex compound A$-$R containing other adsorbed atoms if complete dissociation of A$-$R occurs at the catalyst surface during the course of the reaction. In this case the heat of dissociation of A$-$R enters the expression for the heat of reaction, but the value of $Q_{A-[K]}$ does not change, as can be seen from a comparison of reaction (1) and the reactions:

$$x[K] + A - R = [K]_x A + R; \tag{14}$$

$$y[K] + A - R = [K]_y R + A; \tag{15}$$

$$(x + y)[K] + A - R = [K]_x A + [K]_y R. \tag{16}$$
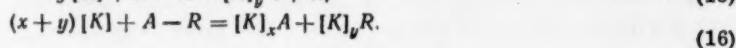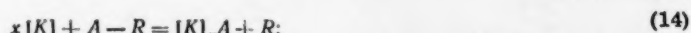
If complete rupture of the A$-$R bond does not occur in the course of reaction at the surface, the values of $Q_{A-[K]}$ may vary. However, over metal catalysts the proportion of bonds broken on adsorption is 0.9-1 [14], so that the variation must be small in comparison with the values of $Q_{A-[K]}$.

We express our deep thanks to A. A. Balandin for his interest in our work.

SUMMARY

Calculations were made of the energy of the bond formed by carbon with the surface of a nickel catalyst on the assumtion that the excess of free energy of the surface compounds is determined mainly by the excess of free energy of the surface of the catalyst.

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*Original Russian pagination. See C. B. Translation.

STRUCTURES OF N-METHYLNICOTONE AND Py-N-METHYLMETANICOTONE

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In 1925-1926 Karrer and co-workers oxidized the Py-methiodide of nicotine (Py = pyridine) and obtained the so-called N-methylnicotone (m. p. 85°), to which they assigned the structure 1-methyl-3-(1-methyl-2-pyrrolidinyl)-2-(1H)-pyridone (I) [1]. The authors based their conclusion on the identity of the chloropyridine carboxylic acid which they obtained from (I) with 2-chloronicotinic acid [2]. Guided by this, we described [3] the product of cleavage of the pyrrolidine ring in the substance of m. p. 85°, the so-called Py-N-methylmetanicotone, as a 3-substituted 1-methyl-2(1H)-pyridone (II). However, following the appearance of an abstract of a paper by Tatsuno [4], we had to return

(I) (II)
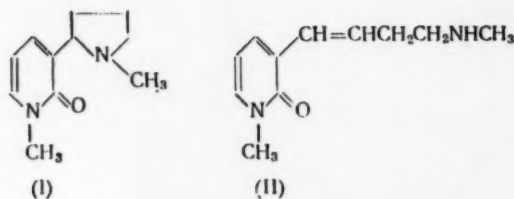
to the question of the structure of the original N-methylnicotone, and therefore to that of Py-N-methylmetanicotone. Tatsuno describes the product of the oxidation of the Py-N-methylnicotinium salt which he isolated [liquid, b. p. 165-170° (7 mm) as 1-methyl-5-(1-methyl-2- pyrrolidinyl)-2-(1H)-pyridone (III); this view is supported by the value that he found for the dipole moment and also by the fact that another analogous nicotine salt (Py-N-phenethylnicotinium bromide) gives the corresponding 5-substituted 2(1H)-pyridine (IV) when oxidized under the same conditions [5]. A similar point of view on the point of attack of the oxidizing agent on the nicotinium salt was expressed

(III) (IV)
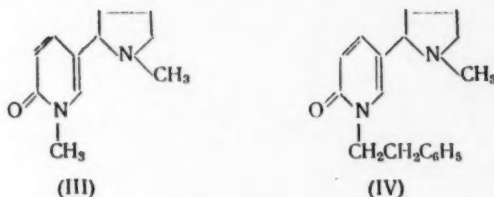
earlier by Sugasawa and Kirisawa [6], who then pointed out that the direction of the oxidation of three-substituted pyridinium salts depends on the nature of the substituent and, of course on the oxidation conditions.* In view of the above-cited facts, it was desirable to carry out the oxidation of the Py-N-methylnicotinium salt under Tatsuno's conditions and compare the compound formed with Karrer's N-methylnicotone. This became

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* For fuller data on this question see Thygaraian's review [7].

possible when, on our request, Tatsuno sent us a reprint of his paper, which was published in Japanese.* After vacuum distillation, the product obtained by us in this way crystallized out and was found to be identical both with respect to the melting point of the base (85°) and with respect to the melting point of the picrate with the above-mentioned Karrer's compound.

To make a final choice between formulas (II) and (III), we decided on a method of proof analogous to that used by Sugasawa and Tatsuno [5] in the investigation of the product of the oxidation of Py-N-phenethylnicotinium bromide: Hofmann cleavage of the Py-methiodide of N-methylnicotone with subsequent oxidation of the resulting dibase with potassium permanganate. We then isolated, though admittedly only in low yield, 1,6-dihydro-1-methyl-6-oxonicotinic acid (VIII), m. p. 240°, which has been described by various investigators [8, 9]. The same acid was isolated by us from the aldehyde (X), which was isolated after the ozonization of the base (IX). In this way we determined the structure (VI) for the methiodide taken in the cleavage reaction, so that the structure (V) for Karrer's N-methylnicotone is 1-methyl-5-(1-methyl-2-pyrrolidinyl)-2(1H)-pyridone. Py-N-Methylmetanicotone, which we described previously [3], must then have the structure (IX), 1-methyl-5-(4-methylamino-1-butenyl)-2(1H)-pyridone.
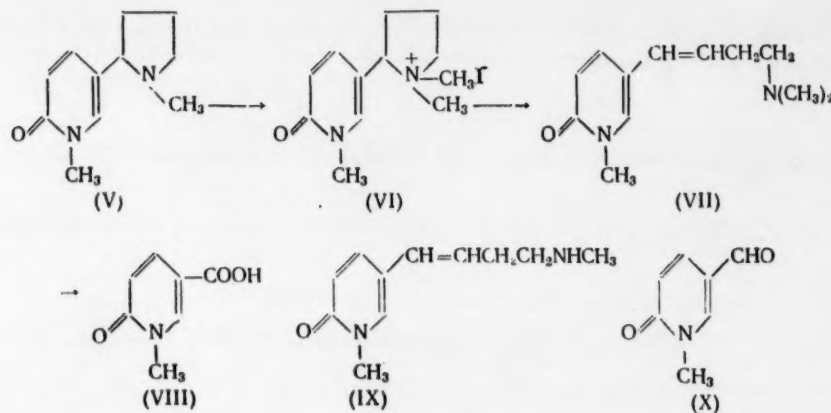
EXPERIMENTAL

1-Methyl-5-(1-methyl-2-pyrrolidinyl)-2(1H)-pyridone (V). 1) By the method described by Karrer [1] we prepared a crystalline product, m. p. 86° after crystallization from heptane. 2) Product (V), prepared under the conditions described by Tatsuno [4] was first obtained in the form of an oil, which was distilled twice under reduced pressure (7 mm; b. p. 168-172°), after which it crystallized out (m. p. 82-85°); after crystallization from heptane it had m. p. 85°, undepressed by admixture of the substance obtained by Karrer's method.

Methiodide of 1-methyl-5-(1-methyl-2-pyrrolidinyl)-2(1H)-pyridone (VI). This was prepared by heating 10 g of N-methylnicotone (V) with methyl iodide (4 ml) in alcohol. Crystallization from alcohol gave 14.6 g (84%) of crystals of m. p. 210-211°. Found: C 42.92; 43.08; H 5.67; 5.94; I 37.42; 37.94%. $C_{12}H_{19}ON_2I$. Calculated: C 43.11; H 5.69; I 38.02%.

5-(4-Dimethylamino-1-butenyl)-1-methyl-3(1H)-pyridone (VII). This was prepared from the methiodide (VI) (12.5 g) by the usual Hofmann cleavage. The dark-colored oil obtained was vacuum-distilled with passage of a stream of dry nitrogen. We collected 6.4 g (83%) of light-yellow oil, b. p. 163-163.5° (1 mm); on standing it darkened rapidly. Found: C 69.14; 69.09; H 8.79; 8.89; N 13.48; 13.28%. $C_{12}H_{18}N_2O$. Calculated: C 69.9; H 8.74; N 13.59%.

Oxidation of 5-(4-dimethylamino-1-butenyl)-1-methyl-2(1H)-pyridone (VII). (VII) (3.1 g, 0.015 mole) was dissolved in 300 ml of pure dry acetone and oxidized by the addition of $KMnO_4$ powder. The precipitate was filtered off, suspended in water, and brought into solution by the passage of sulfur dioxide. From the acetone filtrate we isolated 1.7 g of the original base. The aqueous solution was evaporated, and the dried residue was extracted with absolute alcohol. From the alcoholic solution we isolated 0.3 g of crystals of the acid (VIII).

* We take the opportunity of again expressing our thanks to Tatsuno.

m. p. 234-236°; yield 25% on the amount of (VII) that reacted. After recrystallization it had m. p. 238° (needles from alcohol). For the melting point of 1,6-dihydro-1-methyl-6-oxonicotinic acid the literature gives 238° and 240° [8, 9] (the melting point of 1,2-dihydro-1-methyl-2-oxonicotinic acid is 183° [10]).

Ozonization of the dihydrochloride of 1-methyl-5-(4-methylamino-1-butenyl)-2(1H)-pyridone. The dihydrochloride of the base (IX) (2.65 g) was ozonized under the conditions described by Gol'dfarb and Karaulova for 3-[4-(acetylmethylamino)-1-butenyl]-2-aminopyridine [11]. We isolated 1,6-dihydro-1-methyl-6-oxo-nicotinaldehyde (0.2 g), m. p. 118.5-120° (from octane). Found: C 60.94; 60.75; H 5.25; 5.11; N 10.16; 10.31%. $C_7H_7O_2N$. Calculated: C 61.31; H 5.11; N 10.22%. The dinitrophenylhydrazone has m. p. 278-280°.

The aldehyde (X) (0.1 g) was oxidized with silver oxide in alkaline solution; after the separation of the precipitate of silver from the solution, we isolated fine needles (0.08 g), m. p. 236-237°, undepressed by admixture of the acid (VIII) obtained as described above. Found: C 54.86; 54.94; H 4.87; 4.71; N 9.05; 8.99%. $C_7H_7O_3N$. Calculated: C 54.90; H 4.58; N 9.15%.

SUMMARY

The structures of N-methylnicotone and Py-N-methylmetanicotone are, respectively, 1-methyl-5-(1-methyl-2-pyrrolidinyl)-2(1H)-pyridone and 1-methyl-5-(4-methylamino-1-butenyl)-2(1H)-pyridone.

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* Original Russian pagination. See C. B. Translation.

PRELIMINARY RESULTS OF A CHEMICAL STUDY OF THE ROOTS OF ARALIA MANSHURICA

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Aralia manshurica (family, Araliaceae) is a small tree which grows in the Primorskii region. Aqueous extracts from the roots of Aralia manshurica have a pharmacological action similar to that of ginseng, which belongs to the same family (Panax ginseng; family, Araliaceae) [1]. No data have been published on the chemical composition of the roots of the Aralia manshurica. As the question of the chemical nature of the substances responsible for the well-known stimulating action of preparations of ginseng and other araliaceae is of great interest, we began a chemical study of the roots of Aralia manshurica.
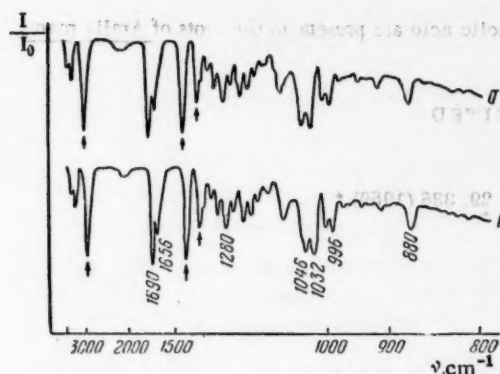

Fig. 1. Infrared spectra of sapogenin isolated from Aralia manshurica (I), and that of oleanolic acid (II).

The investigation was carried out on three samples of roots: 1) roots from the collection of the 1956 expedition of Vilar; 2) roots from hothouse plants (Vilar, 1957); and 3) roots prepared at the Khabarovsk Main Pharmaceutical Administration in 1958. All the samples were found to be identical in composition.

Preliminary investigations by paper chromatography on extracts of the roots obtained with various solvents showed the presence of an extremely complicated mixture of substances, which had already been noted in investigations on ginseng. As well as a considerable amount of reserve sugars, a certain amount of flavanoids, etc., in the aralia roots, we found a high content of saponins, and preliminary data on the nature of these are given in this note.

The total saponins were isolated from the methanol extract of the roots, and were then treated with chloroform and butyl alcohol; they were obtained as an amorphous substance which was difficult to purify; hydrolysis of this with 5% hydrochloric acid gave a difficultly purifiable prosapogenin. This was given a final hydrolysis with a mixture of acetone and hydrochloric acid, as a result of which we isolated a sapogenin of composition $C_{30}H_{48}O_3$, m. p. 305-308° and $[\alpha]^{20}D + 82.8°$, which corresponds to oleanolic acid. Its identity with the latter was confirmed by complete correspondence of the infrared spectra of the two preparations (Fig. 1).

As a result of the hydrolysis of the total saponins, four monosaccharides were determined chromatographically, and one of these was glucose. These preliminary data indicate that the saponins of Aralia manshurica belong to the group of triterpene saponins, data on which are very limited in the literature. Investigations to establish the structure of the saponin of the aralia are continuing.

EXPERIMENTAL

Isolation of the total saponins. Ground air-dry roots of Aralia manshurica (1 kg) were extracted five times with hot methanol. The combined extracts were evaporated to dryness, and the amorphous residue was dried in a vacuum desiccator; weight 50 g. The product (45 g) was dissolved in 200 ml of the aqueous layer of a chloroform-ethanol-water (3 : 1 : 4) mixture, and the solution was extracted three times with 100 ml portions of the chloroform layer of this mixture; it was then extracted with five 100 ml portions of butyl alcohol. The combined butyl alcohol extracts were evaporated to one-fifth of their original volume, and the crystalline precipitate that formed was filtered off, washed on the filter with butyl alcohol, and vacuum-dried; weight 15.0 g. When heated to 250-288°, the substance decomposed with sublimation of oleanolic acid.

Prosapogenin. The saponins (15.0 g) were dissolved in 250 ml of 0.5% hydrochloric acid, and the solution was heated in a boiling water bath for four hours. The hydrophilic precipitate was centrifuged off, washed with water, and vacuum-dried; weight 6.3 g. The substance decomposed at 250-280° with separation of oleanolic acid.

Oleanolic acid. The prosapogenin (2.0 g) was dissolved in 50 ml of acetone and 5 ml of concentrated hydrochloric acid. The solution was boiled for six hours and then diluted with 100 ml of water; the mixture was extracted twice with ether, and the ether extracts were washed with water and shaken with 5% sodium hydroxide solution. The precipitate was dissolved in 100 ml of 1 : 1 ether-alcohol, the solution was acidified with hydrochloric acid, and solvents were distilled off to give a dry residue. The resulting oleanolic acid was recrystallized twice from absolute ethanol; weight 0.4 g. It had m. p. 305-308°, undepressed by admixture of known oleanolic acid; $[\alpha]^{20}D = + 82.8°$ (c = 0.8 in $CHCl_3$).

For oleanolic acid the literature [2] gives: m. p. 307-308°, $[\alpha]^{20}D + 83.6°$ (c = 0.8).

SUMMARY

It was shown that triterpene saponins derived from oleanolic acid are present in the roots of Aralia manshurica.

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*Original Russian pagination. See C. B. Translation.

CALCULATION OF THE TETRAPHENYLCYCLOBUTADIENE
MOLECULE BY THE MO LCAO METHOD

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In a private communication from Prof. A. T. Balaban (Rumanian People's Republic) the question is raised of the possibility of forming a tetraphenylcyclobutadiene molecule in a certain reaction. In this connection we consider it desirable to give the results of a calculation for this molecule by the simple MO LCAO method with the usual assumptions. The results follow.

1) The molecule has a closed electron envelope in the Hückel sense.

2) The distribution of energy levels is as follows: $\alpha + 2.61\ \beta$; $\alpha + 2.10\ \beta$ (doubly degenerate); $\alpha + 2.05\ \beta$; $\alpha + 1.79\ \beta$; $\alpha + 1.26\ \beta$ (doubly degenerate); $\alpha + 1.11\ \beta$; $\alpha + \beta$ (fourfold degenerate); $\alpha + 0.76\ \beta$; α (doubly degenerate). The remaining (antibonding) levels are arranged on the energy scale so as to be symmetric with the bonding levels about α; α denotes the Coulomb and β the exchange integral.

3) The conjugation energy is $10.08\ \beta$.

4) The gain in energy, as compared with four phenyls and one cyclobutadiene, is $2.08\ \beta$.

5) The gain in conjugation energy, as compared with two stilbene molecules, is $0.34\ \beta$.

Hence, on the basis of this simple calculation, even when the model is assumed to be flat there is no reason to suppose that the tetraphenylcyclobutadiene molecule will be stable. Actually, this molecule cannot be flat because of steric hindrance. It is assumed in the calculation that the skeleton of the molecule has a "propellor" form with the phenyl ring twisted at an angle of 30°46' with respect to the plane of the cyclobutadiene ring. This value is obtained from the assumption that the nuclei of adjacent hydrogen atoms from neighboring phenyl rings are separated by twice the van der Waals radius.

In accordance with [1], the value of the exchange integral between the closest carbon atoms of the phenyl and cyclobutadiene rings is taken to be $\beta \cos^2 30°46'$.

Results of the calculation on assumption of noncoplanarity: $\alpha + 2.51\ \beta$; $\alpha + 2.07\ \beta$ (doubly degenerate); $\alpha + 2.03\ \beta$; $\alpha + 1.80\ \beta$; $\alpha + 1.20\ \beta$ (doubly degenerate); $\alpha + 1.08\ \beta$; $\alpha + \beta$ (fourfold degenerate); $\alpha + 0.81\ \beta$; α (doubly degenerate). The remaining (antibonding) levels are arranged on the energy scale so as to be symmetric with the bonding levels about α. The conjugation energy is $9.54\ \beta$; the gain in conjugation energy, as compared with four phenyl rings and one cyclobutadiene ring is $1.54\ \beta$, and compared with two trans-stilbene molecules it is $0.22\ \beta$.

This shows that, as was to be expected, the conjugation energy is lowered, and the conclusion that the tetraphenylcyclobutadiene molecule is unstable remains valid.

SUMMARY

From the point of view of the simple MO LCAO method, there are no grounds for supposing that the tetraphenylcyclobutadiene molecule would be stable.

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QUESTION OF "BOUND" AND "FREE" WATER

A. I. Gorbanev, Yu. M. Kessler, Yu. M. Povarov,
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To explain the discrepancies between experiment and the Debye-Hückel theory [1] various authors have proposed equations in which the "binding" of water by ions is taken into account. In all these cases this is achieved by the introduction into the equations, in the course of their derivation, of the relation

$$N_1 = N_1^0 - hN_2. \tag{1}$$

in which N_1 is the number of "free" water molecules in the solution; N_1^0 is the total number of water molecules in the solution; N_2 is the number of electrolyte molecules; and $\underline{h}$ is the hydration number. The final equations contain the sum of Debye and supplementary terms, of which some, at least, depend on $\underline{h}$. The value of $\underline{h}$ is chosen empirically from comparisons of the equations with experiment on the assumption that the discrepancy between the theory [1] and experiment is due to a reduction in the number of "free" water molecules. Values of $\underline{h}$ so found lie in the range 0-14. However, the physical meaning of $\underline{h}$ at, e.g., $h < 1$ is quite obscure.

Let us write Eq. (1) in the form

$$N_1 = N_1^0 - N_2 \sum_i \nu_i h_i, \quad h = \sum_i \nu_i h_i. \tag{2}$$

in which ν_i is the number of $\underline{i}$ ions formed by the dissociation of one molecule of electrolyte. In the meaning of Eq. (2), h_i is the number of water molecules firmly bound by the ion. It is well known, however, that even the water molecules that are closest to the ion retain, in general, considerable mobility [2], so that h_i cannot be identified with the coordination number n_i. It is natural to suppose that h_i is proportional to n_i. The mobility of water molecules that are immediately adjacent to an ion must be compared with that of water molecules. This can be done on the basis of the views developed by Samoilov [2]. Let us denote the average times spent by a water molecule in an equilibrium position close to an ion and in an equilibrium position in a water environment by τ_i and τ, respectively. Then, $\tau_i/(\tau_i + \tau)$ and $\tau/(\tau_i + \tau)$ will be the relative times spent by the given molecule in the immediate vicinity of the ion and in a position remote from the ion. Their difference characterizes the degree of "binding" of water by the ion. As we are interested not in the absolute mobility of the molecules, but in its change from the value in the pure solvent, we must write

$$h_i = Kn_i \frac{\tau_i - \tau}{\tau_i + \tau} = Kn_i f_i, \quad f_i = \frac{\left(\tau_i^0/\tau^0\right)\exp\left(\Delta E_i/RT\right) - 1}{\left(\tau_i^0/\tau^0\right)\exp\left(\Delta E_i/RT\right) + 1}, \tag{3}$$

in which K is a proportionality coefficient; $\Delta E_i = E_i - E$, and E_i and E are the values of the corresponding potential

barriers. The value of K can be determined from the condition that $h_i = n_i$ when $\Delta E_i = \infty$, whence $K = 1$. Finally, we obtain

$$N_1 = N_1^0 - N_2 \sum_i \nu_i n_i f_i. \tag{4}$$

Hence

$$h = \begin{cases} \sum_i \nu_i n_i \text{ at } \Delta E_i = \infty, \\ 0 \text{ at } \Delta E_i = 0, \\ -\sum_i \nu_i n_i \text{ at } \Delta E_i = -\infty. \end{cases} \tag{5}$$

It will be seen that $h = n_\pm = \sum_i \nu_i n_i$ only in the limiting case of positive hydration. When $0 < \Delta E_i < \infty$, $h < n_\pm$ and expresses the correction for the effective binding of water molecules by ions. When $\Delta E_i < 0$, $f_i < 0$ and $N_1 > N_1^0$; in this case the ions increase the mobility of the water molecules, which is manifested in an apparent increase in their effective number. When $\Delta E_i = \infty$, $h_i = -\nu_i n_i$, but since [3]

$$n_i = \left(\tau_i^0/\tau^0\right) n \exp\left(\Delta E_i/RT\right), \tag{6}$$

($\underline{n}$ is the coordination of water in water), when $\Delta E_i = -\infty$, $n_i = 0$ and therefore $h_i = 0$. The equation $n_i = 0$ is to be understood in the sense that there are no water molecules in direct contact with the ion. In fact, as $E_i \to 0$ ($\Delta E_i \to -E$) the minimum on the potential curve at a distance of $r_{ion} + r_{H_2O}$ from the ion levels out, and at $E_i = 0$ it ceases to exist. It is doubtful whether this case could ever be realized in practice; in actual cases $\infty > \Delta E_i > -E, E > 0, n_\pm > h > -n_\pm$.

In the calculations we used Robinson and Stokes's equation [4], which is analogous to Bjerrum's equation [5] and passes into the equation of [1] when $h = 0$; we used also Glueckauf's equation [6], which gives results close to those obtained by the equation of [4], but does not pass into the equation of [1] when $h = 0$. Let us calculate ΔE_{Cl^-} from $h_{NaCl} = 3.5$ and $h_{KCl} = 1.9$, taken from [4], assuming the values of $n_\pm$ and $\Delta E_\pm$ from [2] and of n_{Cl} from [7]. Let us find τ_i^0/τ^0 from (6) from the data of [2]. We obtain $\Delta E_{Cl^-} = 0.41$ and 0.64 kcal//g-ion from the data for NaCl and KCl, respectively. These results not only disagree greatly, which should not occur if the discrepancy between the theory of [1] and experiment depended only on its neglect of the "binding" of water by ions, but differ in sign from the values calculated from ion mobilities and diffusion [2]. If, following [4], we consider that $\Delta E_{Cl^-} = 0$, we obtain $\Delta E_{Na^+} = 1.41$ and $\Delta E_{K^+} = 0.79$ kcal/g-ion, whereas, according to [2] the respective values are 0.25 and -0.25 kcal/g-ion. The discrepancy becomes still greater if we determine $\underline{h}$ experimentally on the assumption that the mean ionic diameter in the Debye term is equal to the sum of the crystallographic radii of the ions. This corresponds to the assumption of the penetrability of hydration envelopes of ions and is sensible only in the case of electrolytes consisting of ions having negative hydration. Thus, for KCl at $c = 0.1$ mole/liter we obtain $h = 6$, whence $\Delta E_{K^+} =$ about 1.1 kcal/g-ion. Values of h_i were estimated in [6]; using these values and writing $n_i f_i = h_i$, we find that $\Delta E_{Na^+} = 0.7$, $\Delta E_{K^+} = 0.2$ and $\Delta E_{Cl^-} = -0.2$ kcal/g-ion, which again, however, is in great disagreement with [2] (according to [2], $\Delta E_{Cl^-} = -0.27$ kcal/g-ion). The calculation of $\underline{h}$ gives $h_{NaCl} = -0.99$ and $h_{KCl} = -1.71$, whereas in [6], as also in [4], it is assumed that $h > 0$ in both cases. A negative h_{NaCl} is obtained because the increase in the mobility of water due to the chloride ions is outweighed by the "binding" of water by sodium ions. Hence, the calculations show that taking account only of changes in the mobility of water under the action of ions ("binding" of water) is insufficient to explain the discrepancies between the theory in [1] and experiment. The same conclusion follows from the fact that values of h_i calculated from experiment are not additive, as can be seen from tables of $\underline{h}$ values [4]. It must be mentioned that a purely qualitative indication of the inadequacy of this correction is given in [8].

In principle, Eqs. (3) and (4) permit the determination of coordination numbers and ΔE_i from experimental data on activity coefficients. For this it is necessary to know the contribution of the "binding" of water by ions to the effect, together with ΔE_i or n_i. For the approximate calculation of n_i in the case of strongly hydrated ions, in view of the rapid change of the value of f_i toward unity with increase in ΔE_i, we may assume that $\Delta E_i = \infty$.

SUMMARY

The physical meaning of the correction for the "binding" of water by ions is clarified, and an equation is proposed for its accurate calculation.

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*Original Russian pagination. See C. B. Translation.

LETTER TO THE EDITOR

DEHYDROCYCLIZATION OF PARAFFINS TO CYCLOPENTANES
OVER OXIDE CATALYSTS

E. A. Timofeeva, N. I. Shuikin, and T. P. Dobrynina

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Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk,
No. 3, p. 572, March, 1960
Original article submitted December 7, 1959

In the investigation of the dehydrogenation of 2,2,4-trimethylpentane over an alumina-chromia-potassia catalyst we found that ring closure occurred with formation of a cyclopentane. We proved with the aid of the Raman spectrum and of gas-liquid chromatography that the 98.5-105.6° fraction of the paraffin part of the 2,2,4-trimethylpentane catalyzate (obtained in experiments carried out at 550° at a space velocity of 1.1 hour^{-1}) contained 10-15% of 1,1,3-trimethylcyclopentane. This hydrocarbon was found also in the paraffin part of an isooctane catalyzate obtained at 500°.
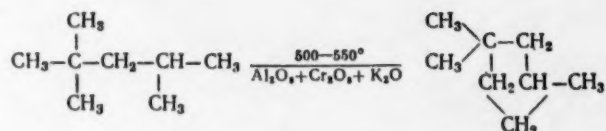
This experimental fact again confirms the possibility of the occurrence of the dehydrocyclization of paraffins to the corresponding cyclopentanes over oxide catalysts. We have previously observed the dehydrocyclization of pentane to cyclopentane over such catalysts [1].

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* Original Russian pagination. See C. B. Translation.

SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY
ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.—Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Metrology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. — Publisher.
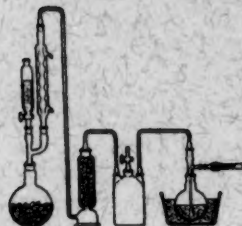
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Tetrahydro-2,5-Furandimethanol
N,N-Diethyltetrahydrofurfurylamine
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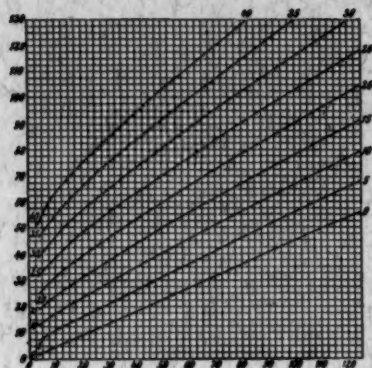
TABLES AND NOMOGRAMS OF HYDROCHEMICAL ANALYSIS

by I. Yu. Sokolov

Translated from Russian

Upon completion of analytical experiments, every research chemist, whether he uses a "test tube" or a "пробирка," must calculate his findings in the international language of figures in two forms (weights and equivalents), and often three (weights, equivalents and percent-equivalents), and then compare experimental data with theoretical values.

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CONTENTS